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RECOVERY, REUSE, AND RECYCLE OF INDUSTRIAL WASTE

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16. ABSTRACT

The major goal of this work is to produce a document useful in planning efforts aimed at elimination of industrial wastes through the application of recycle, recovery, and reuse technology. This goal was accomplished by collecting, reviewing, and evaluating information pertaining to the State-of-the-art for recycle, recovery, and reuse of by-product pollutants using different industrial waste treatment processes. From this information conclusions were made regarding the technological limitations associated with recycle, recovery and reuse of industrial wastes.

The document provides an overview of the applications of the various processes to the recovery of contaminants which may subsequently be recycled or reused.

The pollutants considered in this study are basically organic and inorganic by-products from wastewater effluents, solid residue and gaseous emissions from industrial operations. The first section contains chapters on methodology currently available for recovery of industrial and hazardous waste, and developing technology for recycle, reuse and recovery. The second section contains chapters on 5 technical categories, used for recovery namely, sorption, molecular separation, phase transition, chemical modification, and physical dispersion and separation.

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IWERC is headquartered at Illinois Institute of Technology. Dr. James W. Patterson, Chairman of the Pritzker Department of Environmental Engineering, is the Center Director. The mission of IWERC is to perform fundamental and applied research on industrial waste elimination, reduction or avoidance by recovery, recycle/reuse, and other methods of in-plant management.

Appreciation is expressed to Mr. William A. Cawley, Deputy Director, Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency and Chairman of the IWERC Policy Board.

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CHAPTER 1

SECTION 1

SCOPE OF THE STUDY

1.1 INTRODUCTION

Increased emphasis has been placed on studies of the chemistry, biological effects, treatment, fate, and control of industrial by-product pollutants. Discovery of the presence of such materials at high concentrations coupled with the recognition of their environmental impacts and potential health hazards has led to major legislative efforts which would limit their entrance into the environment. In addition, there is an increased interest to ensure the continued viability of domestic minerals (which constitute most of the raw materials for various industrial operations), minerals economy, and the maintenance of an adequate mineral base. The environmental regulations prohibiting the discharge of major pollutants from industrial activities, coupled with the need for conservation of raw materials has led to consideration of the recycle, recovery, and reuse of waste products. The recycle, recovery, and reuse alternative is doubly advantageous since it conserves a materials supply which is beginning to be recognized as finite while reducing the quantity of hazardous pollutants discharged into the environment.

The choice between recycle, recovery and reuse of valuable materials from waste and disposal of waste seems to depend mainly on two factors; economics and technology. Economics is probably the most important factor that limits the recycle, recovery, and reuse of industrial by-products. The high cost of recovering low-value materials and the consequent relative unprofitability seem to prevent several industries from adoption of recycle or recovery techniques for waste by-products. The high costs of recycle or recovery techniques, however, can probably be reduced by improving the present day technology. Any such attempts would require the identification of technological limitations associated with the recycle and recovery techniques. So, it is necessary to collect, review, and systematically organize and evaluate information pertaining to the state-of-the-art for recycle, reuse and recovery of by-product pollutants; the efficiency, energy, and resources associated with these processes; and the future needs and demands for reduction, elimination, or reuse of the unwanted by-products. The execution of these processes should result in a collection of information which defines the limiting technology and the energy and economic constraints associated with various techniques and processes, as well as their potential for future development and expansion as valuable waste elimination methods. Such information would be of use to focus future developments in the area of recycle, recovery, and reuse technology aimed at the elimination of industrial by-product waste.

1.2 OBJECTIVES

The major goal of this book is to produce a document useful in planning future efforts aimed at the elimination of industrial wastes through the application of recycle, recovery, and reuse technology. This objective was accomplished by collecting, reviewing, and evaluating information pertaining to the state-of-the-art for recycle, recovery, and reuse of by-product pollutants using different industrial waste treatment processes. From this information, conclusions were made regarding the technological limitations associated with recycle, recovery, and reuse of industrial pollutants.

This study is not meant to provide detailed technical information on the treatment process itself no elaborate discussions on the various applications of the processes. It does however, provide an overview of the applications of the various processes to the recovery of contaminants which may subsequently be recycled or reused.

1.3 ORGANIZATION OF THE BOOK

In this book, an attempt is made to suggest technological limitations associated with unit processes currently or potentially employed for removal of organic and inorganic pollutants from various industrial waste streams. This goal was accomplished by collecting, reviewing, evaluating, and summarizing information pertaining to the state-of-the-art for the recycle, recovery and reuse of pollutants in industrial waste effluents.

The pollutants considered in this study are basically organic and inorganic by-products from wastewater effluents, solid residue and gaseous emissions from industrial operations.

The information collected during the course of this project is summarized and presented under two sections. The first section of the book consists of chapters on the methodology currently available for recovery of industrial and hazardous waste, and developing technology for recycle, reuse, and recovery. The second section of the book contains chapters concerned with 5 technical categories, used for recovery namely, sorption, molecular separation, phase transition, chemical modification, and physical dispersion and separation. This categorization is based on the type of transformation a pollutant would undergo during the waste recovery in a given unit process or operation.

It should be pointed out here that the categorization of unit processes as done above, it quite arbitrary and, needless to say, there might be some overlapping.

In each chapter in the second section individual unit processes are presented with a brief discussion of the process itself, its applications, and the technological limitations associated with the process. If a process is used for removal of both organic and inorganic pollutants (for example, ion exchange), its application and the technological limitations are discussed in the same chapter but under different sections for each type of pollutant. A similar approach is adopted in the case of processes (for example, adsorption) which are based on principles common for the removal of pollutants from both gaseous and wastewater streams.

At the outset, each chapter deals with a process description. This would include the underlying principles of the process, operating characteristics, process configurations, and any unique features of the process. A detailed technical analysis of each and every process was beyond the scope of this book.

Immediately following the process description section, each chapter discusses the limiting technology associated with the concerned treatment process. Conclusions on technological limitations of the process for by-product recovery and reuse are made based upon the literature gathered on the process. Sincere attempts were made to make such conclusions as specific as possible. One of the major problems encountered was the literature pertaining to the processes and techniques employed in recovering industrial by-products which were of a general and somewhat non-technical nature. It was consequently difficult to make specific conclusions on limiting technology based on available technical and performance data. As can be expected, due to proprietary value, technical information on industrial processes is not as extensively available as it is in the case of municipal wastewater treatment processes.

The next section of each chapter deals with application of each process for pollutant removal and recovery from industrial waste streams. The types of industries using the process for pollutants removal are listed in this section. In a number of cases, recovery of by-products is not practiced. It seems that very little technical data pertaining to the recovery of by-products in real-life industrial situation are available. In most cases, even the process performance data are scarce due to the proprietory value of the material. It is also possible that information on recovery of industrial by-products is scant due to the fact that this area has received attention only in recent years.

The last section of each chapter gives a list of the references used in preparing the chapter.

1.4 WASTE CLASSIFICATION FOR RECYCLE, RECOVERY AND REUSE

The quantity and quality of industrial wastes generated by various industries is difficult to identify, however, Jennings (1982) has provided an initial evolution by conducting a national industrial residual flow study. Table 1.1 presents the rank order of industries producing residue. Industrial residuals were defined as those residues that are routed either to unique treatment technologies or to chemical waste disposal facilities and considered "hazardous" under the Resource Recovery Act and The Toxic Control Act. Current data indicates that these constitute about 40% by weight of the total industrial discharge. The remaining fraction is composed of such items as industrial trash, foundry sand, wool waste and slags.

The table shows that 75% of the residual volume is from the chemical, primary metals, and fabricated metals industries.

Jennings was also able to estimate the percentage of residual material as to solids, liquid, or sludges as shown in Table 1.2. Under each category, the residuals were identified by physical and chemical properties (Table 1.3). These tables show that liquids and sludges are a large percent of the total problem. This remains true even when the unidentified category is lumped with the solids.

The miscellaneous special solids category contain wastes such as pesticide solids and containers, explosives, pathogenic wastes, DOT "poisons" and similar residues. The metal solutions and metal sludge categories contain predominantly heavy metal residuals. The liquid categories contain both dilute and concentrated solutions and (where appropriate) non-aqueous liquids. Metals solutions and metal sludges accounted for nearly 15% of the total.

1.5 METHODOLOGY

For the purpose of clarity, it is necessary to define the terms recovery, reuse, and recycle. Recovery is defined as the extract of any pollutant from wastes. The terms reuse and recycle described the manner in which the recovered materials are put to use. Reuse of the material is its utilization for any purpose, whether it is the same or different from its previous use. Recycle will be defined as a specific type of reuse in which the recovered material is reused for the same purpose as that for which it had been used previously.

The effort for this book was divided into two different phases and a summary of these phases is in order.

TABLE 1.1

TOTAL QUANTITY OF INDUSTRIAL WASTE ORDERED BY MANUFACTURING INDUSTRIES THAT PRODUCE HAZARDOUS RESIDUAL

INDUSTRIES	PERCENT OF TOTAL QUANTITY*	
CHEMICALS	37.6	74.4
PRIMARY METALS	29.1	
FABRICATED METALS	7.7	
MACHINERY	6.5	22.9
PAPER	4.6	
TRANSPORTATION	4.0	
FOOD	2.7	
PETROLEUM	2.4	
STONE	2.0	
ELECTRICAL	0.7	
RUBBER	0.7	2.6
LEATHER	0.5	
LUMBER	0.4	
INSTRUMENTS	0.3	
MISC. MANUFACTURING	0.2	
FURNITURE	0.2	
TEXTILES	0.2	
PRINTING	0.1	
TOBACCO	<0.1	
APPAREL	<0.1	

---

[*] TOTAL = 100% of 27.8 million tons of wastes reported from 21 states.

TABLE 1.2

PERCENTAGE OF RESIDUAL TYPE IN EACH LEVEL I WASTE CLASSIFICATION

CLASSIFICATION	PERCENT OF TOTAL* IN CLASS
SOLIDS	13.9
LIQUIDS	54.4
SLUDGES	23.8
UNIDENTIFIED	7.9

*Total = 100% of 15.4 million tons of hazardous wastes reported from 30 states.

TABLE 1.3

PERCENTAGE OF RESIDUAL TYPE BY CHEMICAL CHARACTERISTICS

SOLIDS	PERCENT OF TOTAL[1] IN CLASS
ORGANIC SOLIDS	11.8
INORGANIC SOLIDS	28.0
MISCELLANEOUS SPECIAL WASTES	60.2

LIQUIDS	PERCENT OF TOTAL[2] IN CLASS
HALOGENATED ORGANICS	1.0
NON-HALOGENATED ORGANICS	8.6
ACIDS	34.8
CAUSTICS	18.8
METAL SOLUTIONS	11.4
OILS & OILY WASTES	7.6
MISCELLANEOUS LIQUIDS	17.8

SLUDGES	PERCENT OF TOTAL[3] IN CLASS
ORGANIC SLUDGES	41.8
INORGANIC SLUDGES	33.5
METAL SLUDGES	24.7

---

1. Total = 100% of 2.1 million tons of hazardous wastes reported from 21 states.
2. Total = 100% of 8.2 million tons of hazardous wastes reported from 23 states.
3. Total = 100% of 3.6 million tons of hazardous wastes reported from 19 states.

1.5.1 Phase I. Literature Collection

This phase consisted of a thorough collection of literature dealing with information on technology which has or may have application in the areas of recycle, recovery and reuse of by-product wastes as well as information directly related to the industrial by-product materials themselves.

The literature search was approached with the following basic questions in mind: (1) What wastes are presently produced as industrial by-products? (2) What methods can be applied to these wastes to bring about their elimination through recycle, recovery and reuse?

Many sources are available which contain information pertinent to the project, and the tools to facilitate its collection. Sources include journals, reports, books, and the proceedings of conferences and symposia. In order to amass the largest collection of relevant information in the short period of time available, it was necessary to make use of on-line computer literature searches, published literature searches, collections of abstracts, and the literature reviews which appear periodically in certain journals.

On-line computer literature searches (for example, The EPA Computerized Literature Search System) were used to access data bases and provide bibliographic information in response to specific questions. Published literature searches such as those produced by The National Technical Information Service (NTIS) were valuable during the course of the project. Over 1,200 abstracts concerning recycle, recovery and reuse were collected from the Engineering Index.

1.5.2 Phase II. Literature Categorization

During this phase, the abstracts collected from Phase I were reviewed and articles relevant to the project objectives were collected. Information collected from computer searches and published bibliographies were carefully reviewed and pertinent articles obtained.

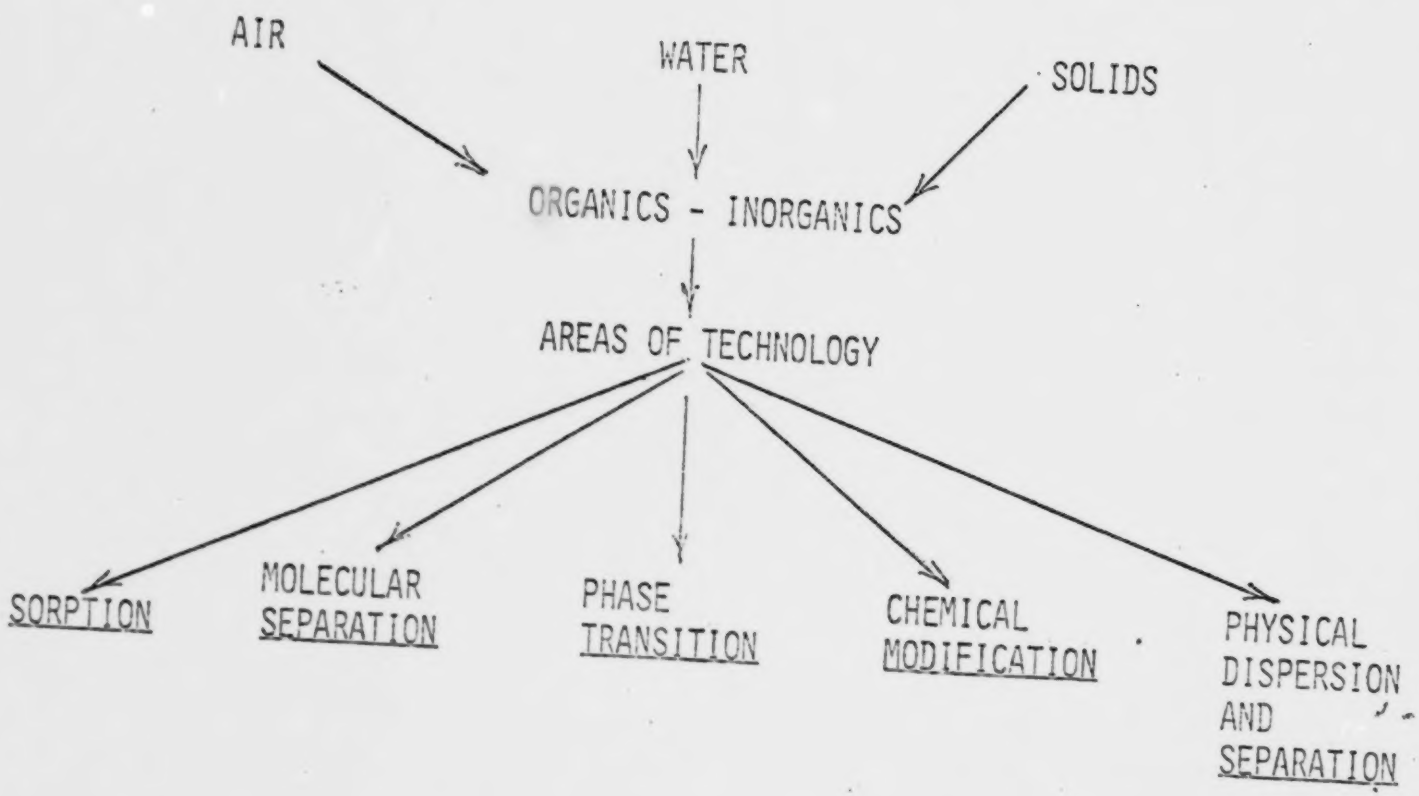
A review of collected literature indicated that the categorization of literature can be based upon one of the three following approaches: a) an industry-by-industry, b) process-by-process, c) material-by-material.

An industry-by-industry approach would have required a classification of industries and their respective wastes and an evaluation of the several possible methods by which these wastes could be treated. It seemed that several industries using a given treatment process had similar technological limitations in terms of recovery of their by-product pollutants. So the same conclusions on limiting technology would have to be repeated for a number of industries for a given treatment process.

If the literature categorization had been based on materials, the waste by-products would require initial identification followed by studies of various processes suited for their recovery and reuse. A careful evaluation of the collected literature indicated that the limitations of technology are more dependent upon the treatment process itself than on the type of waste or type of pollutant treated. It was therefore decided that for the purpose of this project the categorization of literature would be based on treatment processes.

A schematic of literature categorization used in this project is shown in Figure 1.1. The literature was broadly divided into three major areas; air, water, and solids, each of which deals with two major classes of by-products, namely, organics and inorganics. After the collection of the majority of material required by the project had been accomplished, the following tasks were carried out.

FIGURE 1. LITERATURE CATEGORIZATION


AIR
WATER
SOLIDS
ORGANICS - INORGANICS
AREAS OF TECHNOLOGY
SORPTION
MOLECULAR SEPARATION
PHASE TRANSITION
CHEMICAL MODIFICATION
PHYSICAL DISPERSION AND SEPARATION

A total of 18 processes which are believed to have the most wide-spread application in terms of removal and recovery of industrial by-products were selected for study in this project. A list of the processes is presented in Table 1.4. These processes are divided into five groups, depending upon the type of transformation the by-product would undergo during the waste treatment in a given unit process or operation. As mentioned earlier, the five groups of processes are: sorption, molecular separation, phase transition, chemical modification, and physical dispersion and separation.

After the identification of the unit processes listed in Table 1.4, a research specialist was assigned to a unit process. Each treatment process was evaluated according to the following outline:

I. The Process
II. Limiting Technology
III. Recycle, Recovery, and Reuse Applications
IV. References

It should be pointed out here that the references given at the end of each chapter are listed in alphabetical order. Attempts were made to obtain as many references as possible from recent years. The references are classified into four categories:

1) Titles read: Only the titles of the articles were read for the references under this category. No attempts to obtain the abstracts or the original articles were made.
2) Abstracts read: Under this category of references only the abstracts of the articles were read.
3) Articles read: In this case the original articles were read.
4) Articles referenced: The articles listed under this category are actually referenced in the text.

TABLE 1.4 TREATMENT PROCESSES SELECTED

SORPTION	MOLECULAR SEPARATION	PHASE TRANSITION	CHEMICAL MODIFICATION	PHYSICAL DISPERSION AND SEPARATION
ABSORPTION	REVERSE OSMOSIS	DISTILLATION	CHEMICAL REACTIONS	DEWATERING
ADSORPTION	ION EXCHANGE	EVAPORATION	THERMAL REACTIONS	FILTRATION
	ULTRAFILTRATION	CONDENSATION	CEMENTATION	FLOTATION
		REFRIGERATION		DROPLET SCRUBBING
				EMULSION
				LIQ-LIQ EXTRACTION

The references listed under the first three categories are not always quoted in the actual text portion of the chapters. These are, however, included in the references section of each chapter because it was felt that they are related to the information presented in the text and the reader may refer to these, if interested.

1.6 SUMMARY AND CONCLUSION

In this study an attempt was made to collect, review, and systematically organize and evaluate information pertaining to the state-of-the-art for recycle, reuse, and recovery of industrial pollutants through the use of various waste treatment processes and to suggest technological limitations associated with these processes.

At the present time, economics seems to be considered a major factor in deciding if recycle, recovery and reuse of industrial pollutants are worthwhile. Needless to say, current economic costs do not include the 'hidden' costs to society of environmental pollution and depletion of natural resources. However, if the waste treatment technology is improved to a level where economics does not become the limiting problem, recycle, recovery and reuse of industrial pollutants would become feasible.

Generally, most of the processes discussed in this report are well-developed and proven to be successful for effective removal of pollutants they are designed to treat. However, a majority of processes are not either economically or technically effective for recovery of by-product pollutants. For example, precipitation is an effective process for removal but not for recovery of heavy metals. A majority of industrial wastes receive precipitation treatment but in most cases the resulting sludges are disposed of without recovery of metals because of economic constraints.

In the case of processes such as evaporation, there seem to be no insurmountable technical problems, however, operational difficulties, such as crystal formation and scaling seem to limit the recovery application of the process in various industrial operations.

Some of the processes (e.g., cementation) studied in this project are at an infant stage while some others are very well developed (e.g., activated carbon). In the case of cementation, although the process is well developed and commonly used in hydrometallurgical operations, it has not been tested on pilot and full scale at a number of municipal waste treatment facilities. However, its application to industry to date has been limited and there is a large scope for research in this area. Even though major advances have been made in the area of activated carbon technology, fundamental research on adsorption/desorption mechanisms is warranted, which would lead to improved removal and recovery of organic and inorganic compounds.

As mentioned earlier, the second section of this report presents a discussion of several waste treatment processes, their application to industrial operations, and the technological limitations associated with the respective processes. A brief summary of the information contained in the section and the conclusions drawn from it are presented in a process by process order below.

The unit processes considered under the category of sorption are highly developed for removal of organics and inorganics from both gaseous and wastewater effluents. The process of absorption for removing and recovering gaseous pollutants seems to be most efficient when the pollutants are quite soluble in the absorbent and when the absorbent is relatively non-volatile, non-corrosive, and has low viscosity. The rates of mass transfer between the gas and the absorbent are primarily determined by the amount of surface area available for contact. The contact between the gas and liquid solvent are most commonly achieved in plate and packed towers. Absorption of pollutants (such as phenolic compounds, hydrocarbons, H_2S, SO_2, etc.) followed by desorption constitutes a cyclic operation which allows reuse of the sorbent and acts as a device for separation and concentration of the selected gas.

The process of adsorption in the area of air pollution is used for removal of odors, hydrocarbons, Hg, SO_2, and NO. The principal adsorbents are activated carbon, silica gel, activated alumina, and synthetic zeolites. In the recovery of organic gaseous pollutants, activated carbon has been by far the most effective adsorbent used. The recovery of organic compounds after breakthrough has been reached is generally achieved by stripping. The conventional methods of regeneration of air pollutants involve heated air, heated inert gas or heated steam whereas thermal reactivation, steam regeneration, and acid or alkaline regeneration are used for recovery of organics or inorganics from adsorbates used in wastewater treatment.

The technological limitations associated with sorption process are summarized in Table 1.5.

TABLE 1.5 LIMITING TECHNOLOGY FOR SORPTION PROCESSES

ABSORPTION:	
	SOLUBILITY OF GAS IN THE LIQUID
ADSORPTION:	
	UNDERSTANDING OF FUNDAMENTAL MECHANISMS OF REMOVAL
	REGENERATION PROCESSES
	LACK OF COMPREHENSIVE PREDICTIVE MODELS

Of the three processes considered under molecular separation, ion-exchange is a well established process and has been used in industrial operations for a long time whereas the membrane processes such as reverse osmosis and ultrafiltration have received attention only in recent years.

During the process of ion exchange, undesirable ions from a waste stream are transferred on to the ion exchange material, such as synthetic resin, which may be regenerated. Through regeneration, the ions may be recovered in a concentrated stream, and the ion exchange material is made available for further use. Recovery of chromic acid and valuable metals such as chromium, nickel, silver and gold from plating industry effluents is possible. Resins of the macromolecular type have become more common in recent years because of their relatively higher resistance to fouling.

Membrane processes are operated by hydraulic pressure and remove solution components largely on the basis of molecular size and shape involving neither a phase change nor interphase mass transfer. These processes are used to remove hazardous materials contained in both liquid waste streams.

Reverse osmosis is generally applied for removal of low molecular weight solutes, such as salts, sugars and simple acids from their solvent where as ultrafiltration is used for separation of higher molecular weight solutes such as proteins, starch, natural gums and colloidal materials such as clays, pigments and microorganisms. The membranes are made from other synthetic or natural polymeric materials.

There appears to be a substantial need for improved membrane technology. Table 1.6 presents the major technological limitations associated with processes studied under the category of molecular separation.

TABLE 1.6 LIMITING TECHNOLOGY FOR MOLECULAR SEPARATION PROCESSES

REVERSE OSMOSIS, ULTRAFILTRATION AND ION EXCHANGE TECHNOLOGY IS LIMITED BY THE BEHAVIOR OF THE SEPARATED MATERIAL AND ITS EFFECT ON PROCESS PERFORMANCE. FURTHER STUDY OF SEPARATION THEORY AND BETTER UNDERSTANDING OF THE CAUSES OF PROCESS FAILURE ARE NEEDED.

The processes considered under the category of phase transition are evaporation, distillation, condensation and refrigeration. The first two processes are used for the removal and recovery of wastewater pollutants whereas the latter are for gaseous pollutants. In metal and plastics finishing industries and, particularly the electroplating industry, closed-loop recycling of wastes is achieved by using evaporation as a recovery process. Evaporation is a very costly process, however, it becomes cost-effective as the concentrations of pollutants in the wastes increase and the flow rate becomes low. Multiple-effect evaporators are more common in the electroplating industry because of their relatively lower costs.

Distillation is a process in which the vaporization of a liquid mixture yields a vapor phase containing more than one component. As a unit operation, it has been used successfully either singly or in combination with such operations as direct condensation, adsorption, and absorption for the recovery of organic solvents. Distillation has many applications for compound recovery from industrial wastes. The regeneration of activated carbon may result in a liquid which is distillable for recovery of the organic component. Other applications include recovery of methylene chloride from polyurethane waste, the recovery of organics from plating wastes, and the recovery of waste solvents for reuse in cleaning industrial equipment.

The condensation process is employed by chemical process industries to recover solvents and products which can be recycled to manufacturing processes, and is also used to recover volatile hydrocarbons from fuel-storage operations. It employs either contact or non-contact methods for cooling a vapor to the point where the partial pressure of the condensible component equals its vapor pressure. Less commonly, the temperature of the system is held constant and the system pressure is increased until the component's partial pressure equals its vapor pressure.

The production of cooling or heat withdrawal, may be accomplished by the solution melting, or evaporation of a substance, or by the extension of a gas. The term refrigeration refers particularly to cooling below atmospheric temperature. Refrigeration is one of several competing methods for recovering emissions from bulk liquid transfer and storage operations, and has been promoted for vapor recovery at gasoline loading racks.

Table 1.7 presents the technological limitations of processes considered under the category of phase transition.

TABLE 1.7 LIMITING TECHNOLOGY FOR PHASE TRANSITION PROCESSES

EVAPORATION:	CRYSTAL FORMATION, SALTING, SCALING, CORROSION ENTRAINMENT, AND FOAMING
DISTILLATION:	ENTRAINMENT EFFECTS ON ATTAINABLE PURITY
CONDENSATION:	LOW REMOVAL EFFICIENCY AT LOW LEVELS OF CONDENSIBLE VAPORS FOULING OF HEAT EXCHANGE SURFACES BY PARTICULATES

Chemical precipitation and reduction are most commonly used to remove and recover metals from industrial waste effluents. Whereas the former process is used by a number of industrial operations to remove various heavy metals, chemical reduction is mostly used to reduce hexavalent chromium to its trivalent form in the plating and tanning industries. The reduction process in this case is followed by precipitation of trivalent chromium with either lime or sodium carbonate.

Chemical precipitation and reduction are most commonly used to remove and recover metals from industrial waste effluents. Whereas the former process is used by a number of industrial operations to remove various heavy metals, chemical reduction is mostly used to reduce hexavalent chromium to its trivalent form in the plating and tanning industries. The reduction process in this case is followed by precipitation of trivalent chromium with either lime or sodium carbonate.

The cementation process, which is widely used in hydrometallurgical operations, is not well developed for the removal and recovery of metals from industrial waste streams. In this process, the ionized metal in solution is converted to its elemental stage by spontaneous electrochemical reaction through oxidation of another elemental metal which is also kept in solution. The process performance can be predicted in terms of electrode potentials. This process is presently in its infant stage and there seems to be a large scope for research and full-scale application in this area.

Catalytic hydrogenation is a useful method for achieving controlled transformation of organic compounds. Using this technique it is possible to saturate organic compounds with hydrogen. Catalytic hydrogenation has been applied in the production of substitute natural gas having a high concentration of methane and ethane. It has also been used to recover hydrogen gas, and to convert the sulfur present in tail gas to hydrogen sulfide which can undergo conversion to elemental sulfur.

A summary of technological limitations associated with the processes involving chemical modifications of pollutants treated is presented in Table 1.8.

The last category of unit processes considered in this study is physical

TABLE 1.8 LIMITING TECHNOLOGY FOR PROCESSES INVOLVING CHEMICAL MODIFICATIONS

CEMENTATION:

- NOT EFFECTIVE FOR LARGE FLOWS DUE TO LONGER CONTACT TIMES REQUIRED
- EXCESS IRON CONSUMPTION RESULTING IN EXCESS IRON SLUDGE REQUIRING DISPOSAL
- THERMODYNAMIC LIMITATIONS FOR ACHIEVING THE DESIRED LOW LEVELS

PRECIPITATION:

- PRESENCE OF COMPLEXING AGENTS
- ACHIEVING OPTIMAL REMOVALS FOR MORE THAN ONE METAL AT ONE pH

REDUCTION:

- HARD TO ACHIEVE INTIMATE CONTACT BETWEEN THE REDUCTANT AND THE POLLUTANT, ESPECIALLY IN CONCENTRATED WASTES
- INTRODUCTION OF NEW METAL IONS WHICH NEED FURTHER TREATMENT FOR REMOVAL

PYROLYSIS:

- LACK OF UNDERSTANDING OF EFFECTS OF PROCESS VARIABLES ON PROCESS PERFORMANCE

CATALYTIC HYDROGENATION:

- RATE OF CHEMICAL REACTION
- RATE OF HYDROGEN TRANSPORT

dispersion and separation. All the unit processes included in this category (except liquid-liquid extraction) are used for removing suspended matter from wastewater or gaseous streams.

Filtration is a physical process in which solids suspended in a gaseous or a liquid stream are separated by passage through a previous medium that separates and retains either on its surface or within itself, the solids present in the suspension. In all filtration processes, a pressure differential is induced across the medium to force the gaseous or liquid stream to flow through it.

In the case of filtration of liquids, either surface filters in which the solids are deposited on the upstream side of the medium, or deep bed filters, which deposit solids within the medium, are used. Surface filters are normally used for suspensions with more than 1% solids whereas dilute suspensions are treated by deep-bed filters. A wide variety of filtration devices are commercially available.

The filter media used for liquid filtration may be a filter cloth, filter screen, a layer of granular media such as sand, lake, coal, or porous ceramics or a barrier composed of a disposable material such as powdered diatomaceous earth or waste ash. Filter media used for filtration of gases may be porous paper, woven and felt fabric filter, or gravel or sand aggregate bed. Filtration has been used for removal of suspended matter from innumerable types of industrial wastewaters and gaseous streams. Multi-media filtration is commonly used for removal of the metal precipitates from wastewater after it has been subjected.

Flotation is a unit operation used to separate solid or liquid particles from liquid phase. In this process, fine air bubbles which are introduced into the liquid phase attach to the particulate matter and, consequently, the buoyant force of the combined particle and gas bubbles becomes large enough to cause the particle to rise to the surface. Three methods of introducing gas bubbles are available: dissolved air flotation, air flotation and vacuum flotation.

The technological limitations associated with processes under the category of physical dispersion and separation are presented in Table 1.9.

The process of liquid-liquid extraction involves separating the components of a liquid-liquid mixture by the addition of another liquid referred to as the solvent, which is immiscible (or only partially miscible) with the initial phase. The solvent is chosen so that one or more of the components of the original solution will transfer preferentially into the solvent phase leaving the others behind in the so-called raffinate. The major applications of this process in wastewater treatment engineering are 1) recovery of phenol and related compounds from wastewaters and 2) removal of water soluble solvents such as alcohol from wastes containing mixed chlorinated hydrocarbon solvents.

TABLE 1.9 LIMITING TECHNOLOGY FOR PHYSICAL DISPERSION & SEPARATION PROCESSES

FILTRATION:

- LACK OF UNDERSTANDING OF PARTICLE/FILTER INTERACTION
- MAINTENANCE OF FILTER IN GOOD CONDITION

LIQ-LIQ SEPARATION:

- SELECTION OF SOLVENTS AND CONTACTORS TO PRODUCE DESIRED RESULTS

REFERENCES

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CHAPTER 2

SECTION 1

INDUSTRIAL TREATMENT OF WASTE FOR RECOVERY, REUSE OR RECYCLE

2.1 INTRODUCTION

Treatment of waste for recycle, recovery or reuse may be chemical or physical and may consist of a sequence of operations. A list of separation methods for liquids and solids is provided in Tables 2.1 and 2.2. The list has been divided into chemical and physical methods and is only an example of the possible methods that can be combined to recover material. Recoverable material may exist in the waste stream in many different forms, for example, as metals or metal oxides. They may exist as acid solutions of metal salts. Therefore, the selection of a recycle process depends on specific character of the waste and requires careful consideration. For the purposes of this work, technologies were grouped by their similarities and not by their ability to accept similar wastes.

2.2 INDUSTRIAL POLLUTION RECOVERY

EPA funded a study of alternatives to conventional pollution control that involves recycle, recovery, and reuse (MRI, 1980). Twenty-five case reports obtained from the pollution control literature for the 1974-1979 period are summarized. The cases come from 11 industries, domestic as well as foreign operations, and from small as well as large companies and one public sanitary district. A roughly equal number of cases deal with predominantly water- and with predominantly air-related cases. Half the cases involve process modification; the rest involve other types of optimization approaches. Most of the pollution control by process change take place in the process-intensive industries, as might be expected--chemicals, paper,

Table 2.1 TREATMENT METHODS FOR LIQUID EFFLUENT

Chemical treatment methods	Example
Absorption	Solvent recovery
Cementation	Copper recovery
Chlorination	Cyanide oxidation
Demulsification	Soluble oil recovery
Electrolytic processes	Metal recovery
Hydrolysis	Cellulose waste
Incineration	Waste oils
Ion exchange	Metal recovery
Neutralisation	Waste acid
Oxidation	Phenol removal
Precipitation	Metals
Reduction	Hexavalent chromium
Physical treatment methods	
Absorption	Removal of volatile organics
Crystallisation	Recovery of inorganic salts
Distillation	Solvent recovery
Evaporation	Sulphuric acid recovery
Filtration	Sewage sludge
Flotation	Dairy wastes
Foam fractionation	Metal separation
Phase separation	Oily wastes
Reverse osmosis	Desalination
Solvent extraction	Metal recovery
Stripping	Ammonia removal

Table 2.2 TREATMENT METHODS FOR SOLIDS WASTE

Chemical treatment methods	Examples/comments
Calcination	Gypsum
Chlorination	Tin removal
Cooking	Inedible offal
Froth flotation	Coal recovery
	Glass
Leaching	Gives an aqueous solution which may be treated as a liquid waste (Table 2.1)
Sintering	Colliery spoil
	Millscale
Physical treatment methods	
Centrifugation	Animal oil separation
	De-oiling swarf
Comminution	Mining wastes
	Cars
Drying	Filter cake
Granulation	Slag
Magnetic treatment	Iron removal from slag
Screening	Clinker

petroleum, metals, and food.

The common characteristic of the alternative approaches is changed in the production process resulting in the elimination rather than the control of pollutants. Wherever pollutants can be eliminated--through changes in the production process, recycling or reuse of captured wastes, recirculation of streams, or some other strategy--the need for and the substantial costs of terminal treatment systems are avoided or minimized.

Identifying characteristics of alternative approaches involve:

1. Recovery and reutilization of waste materials in the process itself, in the production operations that the system serves, or in an unrelated operation;

2. And/or energy conservation components based on overall design, utilization of process heat, energy generation from waste combustion, or combinations of these;

3. And/or use of substitute raw materials in the production process upstream of the "alternative system" in order to make the system more effective;

4. And/or modification of the production process for the same reasons.

Based on the 25 cases selected, seven categories of innovation accommodate all the cases reviewed. These are shown below:

New device
New procedure
New process
Modified process
Process chemical change/elimination
Fuel substitution
Other waste utilization

The largest number of cases involve process modification and changes in process chemicals, but process chemical change/elimination, in this sampling of cases, tends to be linked to other techniques. Fuel substitution, in every case, involves the use of plant or process wastes as a fuel; if this category is combined with other cases of waste utilization, it becomes the

TABLE 2.3

Project	New/Modified Device	New Procedure	New Process	Process Modification	Change/Elimin. of Chemical	Fuel Substitution	Other Waste Utilization	Water Pollution Reduction	Air Pollution Reduction	Less Sludge	Less Solid Waste	Energy Conservation	Water Conservation	Raw Materials Conservation	Small Treatment System	Industry
Oil separator	X				X				X	X		X		X		Metals fabrication
Scrubber-absorber	X			X					X			X		X		Pulp & Paper
Catalytic oxidizer	X								X			X				Plastics
Fat separator	X								X					X		Food
Water conservation		X						X				X	X			Electronics
Fiber recovery		X		X				X						X		Pulp & Paper
Zero discharge		X		X				X				X	X			Construction Products
Steel sludge recovery			X					X	X	X				X		Iron & Steel
Pickle liquor recovery			X					X		X		X		X		Iron & Steel
Sulfur & energy recovery				X					X			X		X		Pulp & Paper
Water conservation	X			X				X				X			X	Pulp & Paper
Air pollution, energy control				X					X			X		X		Packaging
Fume incineration				X		X			X			X				Textiles
Acid recovery				X	X			X		X				X		Electronics
Odor control				X	X				X					X	X	Chemicals
Water conservation				X				X					X		X	Chemicals
Waste reduction				X	X					X				X		Chemicals
Water conservation				X				X					X			Petroleum
Solvent reclamation					X				X	X				X		Electronics
Acid elimination					X			X						X		Electronics
Sludge combustion						X				X	X	X				Waterworks
Metal recovery						X	X			X	X	X		X		Plastics
Energy recovery						X					X	X				Construction Production
Energy recovery						X						X				Pulp & Paper
Wastewater use							X						X			Pulp & Paper

second most common category. In a large proportion of cases (23 of 25), benefits were reportedly realized in two or more categories. In all but one case, the costs of the innovation were lower than the conventional solution by terminal treatment system. An overview of the cases is presented in Table 2.3 showing the technique or techniques used and the benefits achieved. Six of these cases resulted in recovery or recycle of material and provide a good example of the diverse nature of the technology.

1. Fiber recovery. In this case a manufacturer of corrugating medium launched a campaign to capture and to reuse rejected fibers from four different operations. In each case, rejected fibers were captured, reprocessed, and reintroduced into the process at different stages. Resulting final products were tested to determine whether or not the addition of rejects adversely affected product quality. In the production of corrugating medium, waste fibers cause fewer problems than in fine paper or Kraft specialty production.

2. Recovery of steel plant sludges. Large quantities of water are used in hot strip rolling mills in the steel industry for removing fine scale from the metal in forming. Very fine oxides, together with hydraulic oils and lubricating greases released in rolling operations, enter the flume beneath rolling operations with the water. The very fine particles of oxide are coated with oils and greases, and since small size means more surface area per unit of weight, the metals are very contaminated. The oxides are too fine for direct recharging to furnaces and need to be agglomerated by sintering. The heat of sintering causes the oils and greases to vaporize but is insufficient to burn them, hence these hydrocarbons deposit on air handling equipment, collect dust, and increase maintenance costs. Particulate air

pollution control devices also cannot tolerate these oils. For these reasons, iron oxides occurring in rolling operations are not widely used and must be disposed of as sludge.

The recovery process is a multi-stage process for reclaiming oil-free oxides and recovering the oils. Only around 3 percent of the original sludge is disposed of as waste. The sludge undergoes successive separation and washing cycles; oils and greases are washed from the particles and later separated from the wash solution; oxides are screened into coarse and fine grades.

The system produces a product with 31 percent higher iron content than Mesabi Range Fines and 15 percent higher than Marquette Range pellets. Costs of recovery substantially lower than the cost of raw ores or pellets are claimed.

3. Recovery of pickle liquors. An 85,000 ton/year stainless steel annealing-pickling line used Nitric hydrofluoric acid in the pickling operations. Spent pickle baths were neutralized with lime, dewatered, and disposed of--with loss of all the acid and pollution problems attending sludge disposal.

The recovery is accomplished by liquid-to-liquid extraction using an organic solvent, TBP, at a 75 percent concentration in kerosene. The solvent forms adducts with monobasic acids. The acids are stripped from the solvent with water and the solvent is reused. Sulfuric acid is added to increase acid yield. The metal sulfate by-products are neutralized before disposal.

The process recovers about 95 percent of the acid used; as a consequence of the regeneration process, overall acid usage has dropped by 47 percent.

4. Sulfur and energy recovery. In this case the company faced the need to reduce substantially SO_2 levels and odors from a sulfite mill. SO_2 was

emitted from a vent of the spent sulfite liquor evaporator and from the blow tank receiving gases from the digester at intervals of two hours.

The company solved its problem by ducting evaporator SO_2 emissions directly to the mill's acid plant wet scrubber and by absorbing blow tank SO_2 emissions directly in the acid plant. To deal with the blow tank emissions, the company installed a system for cooling and condensing blow tank off gases ahead of absorption in an absorption tower and for recovering heat from the digester blow as an adjunct to gas cooling. Recaptured SO_2 is reutilized in the mill.

5. Air pollution reduction. This is a case where an inefficient system was designed by the original manufacturer to reduce particulate air pollution and to recover energy. The process involved the handling of corrugated board scrap. Waste materials were shredded and then conveyed pneumatically to a roof-mounted cyclone separator over a baling operation. The system created dust, and plant air was exhausted to the atmosphere. The cyclone was sealed and equipped with a dust filtering device. The captured dust is conveyed automatically to the baling system. Filtered air is returned to the plant, and the incoming air volume is adjusted to the operation of the scrap handling system. Incoming makeup air is now heated by spent steam from corrugating machines, heat which had been vented previously.

6. Metal Recovery. A 180 tons per day incinerator was built to destroy plant waste and sludge, produce energy, and recover silver. The plant started operations in 1976; it had been under development for nearly eight years.

The system receives waste from four manufacturing plants, a large office building, and an educational campus. Solid waste is shredded and separated into a light and heavy fraction. The light fraction is burned in a waterwill incinerator; combustion is augmented by burning fuel oil. Flue gases are used to dry sludge generated in a wastewater treatment plant before being burned. Steam generated in the incinerators is used in a turbine to produce electrical power.

Bottom ashes from the system and from the electrostatic precipitator are processed further to obtain silver. Silver is introduced into the system by waste film generated in the production operations.

As these cases illustrate, recovery, reuse, and recycle approaches take many technical forms--the use of new or modified devices and equipment; new processes that replace or augment existing processes; the modification of existing processes by a variety of techniques including changes in raw materials, the elimination of or change in process chemicals, capture and use of waste heat, recovery of solvents, cleansers, and a variety of raw materials, and the substitution of wastes for purchased fuels.

2.3 INDUSTRIAL WASTE WATER RECYCLE

A study conducted at Argonne National Laboratory (Kremek, 1981), identified the technology presently used to allow reuse of watewater from some major industrial categories. The technology available to recovery material from the metal plating and iron and steel industries provide good illustrations as follows:

1. Electroplating

Wastewater from plating processes comes from cleaning, surface preparation plating, and related operations. The constituents in this wastewater include the basic material being finished as well as the components in the processing solutions. Predominant among the wastewater constituents are copper, chromium, nickel, zinc, lead, tin, cadmium, gold, silver, and platinum metals, as well as ions that occur from cleaning, surface precipitation, or processing baths such as phosphates, chlorides, and various metal-complexing agents.

Wastewater from metal finishing processes comes from cleaning, pickling, anodizing, coating, etching and related operations. Predominant among the wastewater constituents are ions of copper, nickel, chromium, zinc, lead, tin, cadmium and ions that occur in cleaning, pickling, or processing baths such as phosphates, chorides and various metal complexing agents.

Table 2.5 lists the variations in wastewater characteristics found by EPA in its survey of the electroplating industry. The table shows variation between plants as well as within each plant.

Table 2.5 Comparison of Raw Waste Streams
from Common Metals Plating

Constituent	Range (mg/l)
Copper	0.032- 272.5
Nickel	0.019-2954
Chromium:	
Total	0.088- 525.9
Hexavalent	0.005- 334.5
Zinc	0.112- 252.0
Cyanide:	
Total	0.005- 150.0
Amenable to chlorination	0.003- 130.0
Fluoride	0.022- 141.7
Cadmium	0.007- 21.60
Lead	0.663- 25.39
Iron	0.410-1482
Tin	0.060- 103.4
Phosphorus	0.020- 144.0
Total suspended solids	0.100-9970

The results of analysis of the specific constituents of raw waste streams, from 50 metal finishing establishments are presented in Table 2.6 through Table 2.7.

Table 2.6 Composition of Raw Waste Streams from Anodizing (in mg/L)

Chromium, total	0.268- 79.20
Chromium, hexavalent	0.005- 5.000
Cyanide, total	0.005- 78.00
Cyanide, amenable to chlorination	0.004- 67.56
Phosphorus	0.176- 33.00
Total suspended solids	36.09 -924.0

Table 2.7 Composition of Raw Waste Streams from Coatings (in mg/L)

Chromium, total	0.190- 79.20
Chromium, hexavalent	0.005- 5.000
Zinc	0.138- 200.0
Cyanide, total	0.005- 126.0
Cyanide, amenable to chlorination	0.004- 67.56
Iron	0.410- 168.0
Tin	0.102- 6.569
Phosphorus	0.060- 53.30
Total suspended solids	19.12 -5275

Table 2.8 presents a summary of a survey showing that a substantial number of evaporation, ion exchange, and reverse osmosis units are currently used in a variety of recovery applications.

Table 2.8 Current Application of Leading Recovery Techniques for Electroplating and Metal Finishing

	Units in Operation		
Application	Evaporation	Ion Exchange	Reverse Osmosis
Chromium plating	158	50	---
Nickel plating	63	38	106
Copper plating	19	--	3
Zinc plating	7	--	3
Cadmium plating	68	--	--
Silver/gold plating	13	20	---
Brass/bronze plating	10	--	---
Other cyanide plating	6	--	---
Mixed plating wastes	---	11	6
Chromic acid etching	6	--	---
Other	16	2	1

2. Iron and Steel

The production of steel involves three basic processes:

1. Coal is converted to coke
2. Coke is combined with iron bearing material and limestone and reduced in a blast furnace to form molten iron and
3. Iron is then purified into steel in an open hearth, basic oxygen or electric arc furnace.

Two of the processes involved in this operation that can be documented to provide product recovery are as follows.

1. Cokemaking

Cokemaking operations include by-product recovery and beehive facilities. Nearly all the metallurgical coke produced in the United States is made in by-product recovery coke ovens.

The by-product recovery process not only produces high quality coke for use as blast furnace or foundry fuels and carbon sources, but also provides a means of recovering valuable byproducts of the distillation reactions. The volatiles are recovered from the gas stream and processed in a variety of ways to produce tars, light oils, phenolates, ammonium compounds, and napthalene (Table 2.9).

Table 2.9 Materials Recovered in By-Product Cokemaking Operations

Material	Extent of Recovery	Use
Crude coal tar	All plants	Resale and/or further processing
Crude light oils	Most plants	Resale and/or reuse
Ammonia and ammonium compounds	Most plants	Recirculation
Phenol, phenolates, carbolates	Most plants steam strip-free ammonia from excess ammonia Half of these plants recovery fixed ammonia	Reuse on-site
Sulphur and sulphur compounds	About 1/3 of the plants desulphurize	Reuse on-site
Napthalene	About 70% of the plants	No information

2. Acid Pickling

During the forming and finishing operations, the steel is exposed to the atmosphere causing an oxide scale to form on its surface. Before further processing, this scale must be removed as it interferes with the application of protective coatings to the steel and for cold rolling. An acid pickling solution is used to remove the scale. Regardless of the type of acid used, sulfuric, hydrochloric or a combination of these two, the spent pickle liquors (SPL) are highly contaminated. Approximately 1.4 billion gallons of spent pickle liquor is generated annually: 500 million gallons of spent sulfuric acid; 800 million gallons of spent hydrochloric acid; and 74 million gallons of combination pickling acids.

Following is an explanation of sulfuric and hydrochloric recovery and regeneration technologies.

> Sulfuric Acid Recovery - The most common treatment method for recovering valuable products from spent sulfuric acid is acid recovery by removing ferrous sulfate through crystallization. Spent pickle liquor, which is high in iron content, is pumped into a crystallizer, where the iron is precipitated (under refrigeration or vacuum) as ferrous sulfate heptahydrate crystals. As the crystals are formed, water is removed and the free acid content of the solution increases to a level where it is reusable in the pickling operation. The crystals are separated from the solution, and the recovered acid is pumped back to the pickling tank. The by-product ferrous sulfate heptahydrate is commercially marketable. The crystals are dried, bagged, and marketed, or sold in bulk quantities. Ferrous sulfate, commonly referred to as "copperas," is used in appreciable quantities in numerous industries, including the manufacture of inks, dyes, paints, and fertilizers. It is also used as a coagulant in water and wastewater treatment.
>
> Hydrochloric Acid Regeneration - The only commercially proven technology to regenerate spent hydrochloric acid is through thermal decomposition. The spent pickle liquor contains free hydrochloric acid, ferrous chloride, and water. The liquor is heated to remove some of the water through evaporation and to concentrate the solution. The concentrated solution is

then further heated to 925° to 1050°C (1700° to 1920°F). At this temperature, water is completely evaporated and the ferrous chloride decomposes into iron oxide (ferric oxide, Fe_2O_3) and hydrogen chloride (HCl) gas. The iron oxide is separated and removed from the system. The hydrogen chloride gas is reabsorbed in water (sometimes rinsewater or scrubber water is used), to produce hydrochloric acid solution (generally from 15% to 21% HCl) which is reused in the pickling operation. There are several types of these "roaster" processes in operation.

References

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Kremer, F., Broomfield, B., "Recovery of Materials and Energy. From Industrial Wastewaters." Argonne National Laboratory, December 1981.

CHAPTER 3

SECTION 1

RESOURCE RECOVERY FROM HAZARDOUS WASTE

3.1 INTRODUCTION

The generation of increasing amounts of hazardous and toxic wastes associated with the nation's rapid industrial expansion represents a problem of increasing public concern. The Environmental Protection Agency, has recently presented statistics indicating that 10-15% of the 344 million metric tons of wet industrial wastes that are produced each year can be classified as being hazardous (US EPA, 1974).

Hazardous wastes have been variously defined. The Resource Conservation and Recovery Act of 1976 (RCRA) defines a hazardous waste in Section 1004(5) as:

- A solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may -
  - Cause or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness, or
  - pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

More recently EPA has attempted to identify hazardous wastes in terms of certain characteristics as (US EPA, 1974):

- ignitability
- corrosivity
- reactivity
- toxicity

Resource recovery is attractive both for economic and environmental reasons. Recovery of waste energy or material value is becoming an increasingly viable option, as ultimate disposal options become more strictly regulated and expensive. The market for recovery has begun to develop an industry, including centralized commercial processing and recovery facilities, and industrial waste exchanges.

Resource recovery typically involves recycle and reuse, either with or without pretreatment before reuse. Each increment of hazardous waste which is recycled has value, plus represents an increment of material not requiring detoxification and/or ultimate disposal.

The State of California has recently reported five alternatives to landfill which are to be encouraged by regulatory and other efforts. In order of preference these are: source reduction by changing industrial processes to generate less waste; waste recycling and resource recovery; physical, chemical, or biological treatment that renders the waste innocuous; high-temperature incineration for many organic compounds; and solidification or stabilization methods that chemically fix or encapsulate the wastes so that they are less mobile in the environment. Since 1977, the State of California has had an active program to investigate the feasibility of recycling hazardous wastes and to develop techniques to encourage such reuse in California. This program includes research and development, and technical liaison through a combined clearinghouse-consultation approach with industry, and has resulted in a successful and growing trend of recycle and recovery. On the basis of experience to date, the State has identified five broad recycling categories of hazardous wastes;

Type I Unused commercial chemicals in packages.

Type II	Process wastes that are economically and technologically feasible for recycle without prior treatment.
Type III	Process wastes that are economically and technologically feasible to recycle if pretreated.
Type IV	Process wastes that are not presently economically and technologically feasible to recycle.
Type V	Wastes that are undesirable to recycle.

Type IV wastes may shift to the Type II or III category as the experience and data base for recycle expands. Type V wastes include those extremely hazardous substances (carcinogens, pesticides) that must be destroyed due to bans or restrictions on their use.

3.2 Resource Recovery

Before specific processes and alternatives for resource recovery are discussed, it is necessary to describe broad strategies for the recovery of economic value from hazardous waste processing. In general, there exist four broad paths whereby recovery of some value from waste may occur:

- Direct recycle for primary (generator) use
- Use by a second industry as a raw material
- Energy recovery
- Utilization in pollution control systems

A given hazardous waste stream may be a potential candidate for recovery by more than one of the above routes; however consideration of the benefits to be derived will provide guidance in determining needed pretreatment methods to be used.

Direct Recycle. One route for reuse of a hazardous waste is the processing of the waste stream to recover materials of value to the industry which generated the waste. For larger generators, strong economic incentives to implement direct recycle options exist. However at smaller generators, the cost of recovery may negate any value to be recovered; here the possibility exists for collection and recovery by a contract processor.

Some instances of direct recycle, to be elaborated upon below, include chromic acid recovery from spent plating bath solutions, and organic solvent recovery from degreasing operations.

Recycle to a Second Industry. By definition, the wastes disposed of by an industry have no intrinsic value to that industry so, that in many cases, direct recycle is not a viable option. However, the waste from a given industry may contain material of value to another industry, and may represent a competitive source of supply of that material, either with or without intermediate purification and/or enrichment.

Example possibilities for secondary recovery include solvent recovery, recovery of phenols from coking wastes, sulfur recovery from stack gas cleanup, and metal and/or acid recovery from various pickle liquors. Industrial waste exchanges perform a secondary recovery function, by accepting wastes from one site, and providing it as a process chemical to another.

Energy Recovery. Many hazardous wastes, particularly those containing organic matter, have sufficient energy value to enable recovery of energy to be economically viable. The most common implementation of this strategy is the use of spent solvents or waste oils for steam generation. An additional, and attractive, option would appear to be the use of waste chlorinated solvents as alternate fuel sources in cement manufacture. Energy recovery may occur at the site of the generator, or at a secondary site.

Recovery for Pollution Control. In some cases, the value of a given waste stream may be realized by using the waste stream in the control of other pollutants, in place of more expensive alternative treatment reagents. The most common use of this strategy is the neutralization of waste by mixing an acidic and an alkaline waste stream. Another promising strategy is the use of waste pickle liquor for hydrogen sulfide or phosphorous control in wastewater treatment plants.

3.3 UNIT PROCESSES USED IN RESOURCE RECOVERY

The treatment which a specific hazardous waste receives prior to resource recovery may consist of a number of discrete unit processes, which depend upon the nature of the material, the nature of the desired end-product and the type and extent of contamination. Many other factors will influence the selection of processes that are chosen, such as economics, geographical considerations, and Federal, State and local environmental regulations. Specific examples will be discussed in a later section when individual wastes are considered. A brief summary of each process, and types of applications that may be important in hazardous waste processing is given in Table 2.

3.4 EXAMPLE RESOURCE RECOVERY OPTIONS

Resource recovery options exist for many of the types of hazardous wastes, and will be discussed in this section.

Recovery from Acidic Wastes. As indicated in Chapter 1, it is estimated that about 35% of all liquid wastes contain acids. In the case of acid recovery from relatively uncontaminated solutions, the purification and recovery of the acid is technically feasible. However, the economics strongly depend on the acid concentration, and local factors, such as transportation costs.

In the case of nitric acid wastes, recovery may be effected by steam distillation. The recovered product, after condensation, consists of a mixture of 68% acid and 32% water, which is the constant boiling point composition. This product may then find numerous industrial uses. The waste from the recovery operations, consisting of still bottoms, would be neutralized and, where necessary, given further treatment, and any residue disposed of in a secure landfill (Ottinger, et al., undated).

In the case of wastes containing sulfuric acid, recovery can be effected if the following requirements are met:

- The recovery operation is near an existing sulfuric acid plant.
- Waste contains more than 70% acid.
- Waste volume is greater than 50 tons/day.
- Organic impurities are low.
- Inorganic impurities are low.

The recovery process involves the use of heat to decompose the acid into sulfur dioxide, which evolves as a gas. The gas stream is then collected and piped to the sulfuric acid manufacturing operation for use as a raw material (Ottinger, et al., undated).

Acid Solutions Containing Metals. Acidic solutions containing metals arise from metal finishing operations; from electroplating operations, both as spent plating solutions and as rinsewaters; from the steel industrial processes. There may be a potential for recovery of either or both the acid and the metal contained in the waste.

In the case of waste pickle liquor, it is possible to use the waste directly in pollution control. The ferrous iron salts that may constitute as much as 15% of the waste, have been useful for the removal of phosphorus from wastewater effluents by precipitation (Ottinger, et al., undated).

Recovery of metals from other wastewaters may be effected by various precipitation or ion exchange processes. These have generally been designed or discussed on a case-by-case basis, with the principal exception of chromium recovery. (Weber, 1972) has outlined a three-bed process for the treatment of chrome plating wastes, involving recovery of treated water strong (4-6%) chromic acid solution, and separated metal sulfates in a regenerant waste stream.

In the case of most other metals, the initial step in recovery from an acidic waste stream would appear to involve neutralization and precipitation. The resulting sludge can then, in some cases, be treated for metal recovery. One process proposed involves the leaching of these sludges with sulfuric acid, and filtration, to remove solid matter, such as calcium sulfate. The filtrate may then be neutralized to pH 3, with an alkali, to precipitate iron hydroxide for recovery. Remaining filtrates can be electrolysed for recovery of metallic nickel and copper. The supernate from the electrolysis operation can then be neutralized with lime to a pH of 9, and cadmium, chromium and zinc recovered from the precipitate. One economic analysis of this process configuration indicated that, for a plant treating 50 tons/day of metal sludge, a net income, exclusive of costs associated with ultimate disposal of residuals, of $572/day was possible (Battelle Memorial Institute, 1974).

In certain cases reductive precipitation of metals from waste streams may be practicable. In the case of chromium, reduction of hexavalent chromium to trivalent chromium, followed by alkaline precipitation produces a sludge containing chromium hydroxide. It has been proposed that this sludge may be treated with sulfuric acid, for the recovery of chromium sulfate, and subsequent reuse in the leather tanning industry (Ottinger, et al., 1973). In view of the geographic concentration of leather tanning in New York, and the proposal for a central treatment facility for this industry (Iannotti, et al., 1979), possible implementation of such a chrome recovery step may be appropriate.

For the recovery of nickel, copper, and silver from wastewaters, reductive precipitation has also been proposed. After silver solutions are contacted with zinc dust, metallic silver can be recovered (Battelle Memorial Institute, 1974). Treatment of wastes containing nickel or copper with iron filings at a pH in excess of 3.5 may also result in the recovery of metallic nickel or copper (Battelle Memorial Institute, 1974).

Acid Solutions Containing Organics

Many wastes fall in this category, ranging from minuscule flows to very large flows and varying from low concentrations of both acids and organics, to very high concentrations of either or both components. The organics may be present either in emulsified form or in dissolved form.

Resource recovery may be directed in one of two directions for waste streams containing substantial quantities of components.

- neutralization of acid and recovery of organics
- removal of trace organics and recovery of acids

Neutralization of acid wastes containing emulsified organics often causes the emulsion to break and allow the separation of a substantial fraction of the organic material which can be removed by skimming or decantation. If the quantity of organics warrants recovery, it may be fractionated and purified by distillation. Otherwise the organic layer can be removed and incinerated. Any residual dissolved organics may be removed by one of several techniques such as adsorption, flotation or extraction, or one of the biological treatment methods. Recovery of grease and oil from acid wastes is often feasible, e.g. acid waste streams from refineries or from electroplating, or metal finishing operations (Hall, 1978; Tabakin, 1978;

Luthey, 1978; Steiner, 1978; Humenick, 1978; Levin, 1981).

If the quantity of organics in acid wastes is small they may be removed by techniques such as adsorption, flotation or extraction. The remaining acid, if in attractive quantity, can be removed and recovered or possibly reused by the techniques discussed earlier in this section. It may be noted that increased attention has recently been given to the recovery of acids from pickle liquor (Wadhawan, 1978).

Acid Sludges

Acid sludges come from a wide variety of industrial processes and vary widely in quantity and composition. They often are highly viscous which makes further processing quite difficult. It therefore, is unlikely that any great potential exists for recovery except in special situations which must be evaluated on a case to case basis.

An exception to the above statement is the case of acid sludges from electroplating operations. These sludges may contain metals together with high concentrations of acids which makes the waste hazardous. Recovery of the metals may be accomplished by extraction with suitable solvents or acids and subsequent recovery of the metals by ion exchange or neutralization, precipitations and filtration. Thus recovery, treatment and disposal can be incorporated in the same process (Gurnham, 1965; Nemerow, 1978; Leonard, 1971).

Acid Gases

The potential for recovery or reuse is small except in some special cases. For instance flue gas is sometimes used to neutralize alkaline liquid wastes, utilizing the acidic components of SO_2 and CO_2 (Nemerow, 1978; Steele, 1954; Cana, 1959; Fisco, 1960). Some instances of HCl recovery by absorption and concentration have also been reported (Nemerow, 1978; Besselievre, 1969; Gurnham, 1955).

Resource Recovery from Alkaline Wastes

Alkaline wastes may be generated in a variety of industries, including electroplating and textiles. Some of these wastes may contain cyanides and metals, as in electroplating; other wastes may contain high concentrations of organics and/or solids, as in textile manufacture. Resource recovery strategies may include recovery of the alkali itself, or recovery of the other materials contained therein. In addition, the possible use of any alkaline material as a scrubber feed should be mentioned, for possible use in the removal of acid gases from incinerator stack gases.

Alkaline Solutions Containing Metals

The major class of wastes of this group is that arising from electroplating wastes containing metal cyanides. This type of waste is widespread in many major industrial centers. A potential exists for resource recovery and various recovery strategies have been described.

Three possibilities for recovery have been described. A simple evaporative distillation to recover water, and concentrated metal cyanide solution can be carried out to permit reuse at the point of generation. (Ottinger, *et al.*, 1973). A second strategy for metal recovery alone involves the addition of metallic iron to the waste, to allow the precipitation of elemental copper and nickel from the solution (Ottinger, *et al.*, 1973). The residual will contain cyanide, which must be further processed prior to ultimate disposal.

Both the metal and the cyanide may be recovered if an ion exchange process is employed. In this case, two different beds are used--an anion exchanger and a cation exchanger, and the waste is passed through the two columns in series. In the cation exchanger, regeneration yields a metal solution, typically metal chloride, if brine is used as a regenerant. In the anion exchanger, use of either caustic or brine as a regenerant will allow recovery of sodium cyanide. The resulting metal chloride stream and sodium cyanide stream may then be used in the plating process, or sold for a secondary use (Ottinger, et al., 1973; Booz Allen Research Inc., 1973).

Alkaline Solutions Containing Organics

If the organic material present in these wastes is at a sufficiently high concentration, and is of a nature where recovery is desirable, then alkaline solutions containing organics may be treated for recovery of the organic fraction according to procedures described in a later section. For several waste streams, however, the nature of the organic contaminant, or its concentration, are such that organic recovery is either not practicable or economic. In these cases, recovery of the alkali might be investigated.

As an example of this possibility, wastes from textile processing may consist of a strong caustic solution, routinely contaminated with hemicellulose. In a full scale installation, use of dialysis for the recovery of a 9-10% caustic solution, free of organic impurities, has been found feasible, and has resulted in a recovery of 200 tons/yr of sodium hydroxide (Iannotti, et al., 1979). It would be anticipated that this technique can be applied to strong alkaline solutions containing organic contaminants, provided that other inorganic contaminants and suspended solids concentrations were relatively low.

Alkaline Sludges

Alkaline sludges may arise in a number of industrial processes. The most common type of alkaline sludges for which resource recovery processes have been proposed is the sludge resulting from chloralkali manufacture. These wastes may contain lead, where the diaphragm cell process is used, and mercury from electrode contamination and brine impurities.

It has been proposed that lead recovery from waste sludges of the diaphragm cell process could be carried out using smelting. The sludge to be treated is dewatered, using coagulants, and filtration, to 25% solids. The dewatered sludge can then be blended with lime, silica, and coke, and smelted in a reducing atmosphere at 1000-1040°C for lead recovery in the ash. Using this process, air pollution controls on the smelter would be necessary, and the filtrate from the dewatering operation could be sent to the main water treatment plant (Shaver, et al, 1975). The estimated cost of this process was $0.81/metric ton of chlorine produced.

Two mercury recovery processes for chloralkali sludges have been proposed, and are currently in use in industrial applications. Georgia-Pacific in Bellingham, WA has been reported to use a dewatering process, followed by roasting to recover mercury. The mercury vapor is recovered from the combustion gases by condensation and demisting. The data from the full scale installation permits a cost estimation, including recovery of mercury, of $2.50-2.90/metric ton of chlorine produced (Shaver et al., 1975).

Mercury recovery from a similar waste by a non-thermal process is practiced at the BASF Wyandotte plant, Fort Edwards, WI. The brine purification muds are acidified to pH 2 with waste concentrated sulfuric acid, and calcium carbonate is allowed to precipitate. The mixture is then treated with sodium hypochlorite at pH 6-7 to dissolve the mercury from the sludge.

Vacuum filtration to remove the remaining low-mercury solids for disposal, and collection of the mercury-laden filtrate is then performed. The filtrate is then combined with other mercury laden wastes, and treated with sodium bisulfite, sulfuric acid and sodium hydrosulfide for about 16 hours to precipitate mercuric sulfide. The mercuric sulfide can be recovered as a filter cake by leaf filtration. The effluent can then be discharged, after batchwise monitoring for mercury levels. The mercuric sulfide may be used offsite, or may be dissolved in sodium hypochlorite and the solution recycled to the main plant brine circuit. Operating data from full scale installation indicate a net cost of $6.90/metric ton of chlorine produced (Shaver *et al*., 1975).

Resource Recovery from Other Inorganic Wastes

Various waste streams may be generated that contain hazardous inorganic materials such as salt solutions, solid salts, metals and non-metals. A wide range of materials and concentrations are encountered, and the possibility of recovery or reuse must be evaluated for individual situations.

Salt Solutions

There does not appear to be a high potential for recovery from wastes of this type. Some process solutions may contain hazardous salts in sufficient concentrations to warrant recovery, such as fluorides from smelting operations (Gurnham, 1965). Various concentration techniques such as evaporation may be necessary as pretreatment and they are usually expensive because of investment costs and high heat costs. Reuse of waste salt solutions can sometimes be practiced, either within the same process from which waste originated or in neighboring processes or other industries.

Solid Salts

Various metal-finishing industries discharge batches of salts used as molten salt baths for heat-treating. These baths often contain cyanides, fluorides, and other salts with toxic properties. Recovery from these mixtures is possible by dissolving, filtering and recrystallizing the salts. Such processing is, however, unlikely to be cost effective (Ottinger _et al_., 1973; Shaver _et al_., 1975; Genser _et al_., 1977).

Metals

The electrolytic refining of copper results in the generation of an anode mud which contains hazardous materials such as arsenic, antimony, nickel, selenium and tellurium. The concentrations of these materials may be high enough to justify extraction and recovery of these materials by ion exchange or electrolysis (Gurnham, 1965).

Some metal refineries and other industries generate metallic dusts which are usually water scrubbed for removal of entrained solids. Recovery from the scrubber water by filtration is practiced (Leonard _et al_., 1977).

Wastes discharged from some chlorine-alkali electrolytic cells often contain substantial amounts of mercury. The mercury can and should be recovered by controlled incineration or retorting followed by condensation of the mercury combined with vapor cleanup with mist eliminators, adsorption and activated carbon or scrubbing with hypochlorite solutions (Ottinger _et al_., 1973; Shaver _et al_., 1975; Booz Allen Research Institute, 1973).

Lead is frequently recovered from storage batteries and other waste materials. Carefully controlled smelting or burning techniques have been used to recover the lead. The value of lead makes its recovery attractive (Gurnham, 1965; Battelle Memorial Institute, 1974).

Non-Metals

A potential exists for the recovery and reuse of sulfur from a number of common hazardous waste streams. Many processes found in such industries as the coke and steel industry, tanneries and various chemical industries generate toxic sulfur compounds. These materials often appear in alkaline scrubbing wastes or other waste solutions. The sulfur compounds can often be concentrated by steam stripping, converted to hydrogen sulfide and then reduced to elemental sulfur by the Claus Process or one of its modification (Ottinger et al., 1973).

Resource Recovery from Concentrated Organic Liquids

The potential for resource recovery from concentrated organic liquid wastes arises from the economic, material and energy values resulting from the presence of certain specific organic materials, such as solvents, within the waste stream. For lightly contaminated material, resource recovery is relatively easier than for heavily contaminated waste. However, in general, all strategies embody some degree of purification, which results in both recovery of a more usable product, and partial detoxification and volume reduction of the residual waste.

Lightly Contaminated Wastes

In a wide variety of industries, recovery of solvents from lightly contaminated wastes is feasible, and is currently practiced. It has been estimated that some pharmaceutical companies recycle over 99% of the hazardous solvents which they use (Booz Allen Research Institute, 1973). In the electronic components industry, surveys indicate that over half of both the halogenated and non-halogenated solvents are segregated for reclamation (Peters *et al.*, 1977). A wide variety of solvents and other organics may thus be reused, including the halogenated methanes and ethanes (FEA, 1976).

Techniques used for solvent and organic recovery vary with the nature of the waste and the product desired. In some cases, relatively clean solvents may be wasted, and simple repacking for use by other commercial users is adequate (Peters *et al.*, 1977). More commonly, distillation and recondensation are used to recover desired solvents (Peters *et al.*, 1977; FEA, 1976). Several commercial reclamation services employ extensive distillation or fractional distillation processes for solvent recovery.

A detailed process design has been published, involving multiple distillation and condensation steps, which is claimed suitable for separation and recovery of the following organic solvents: methylene chloride, chloroform, methyl chloride, chloroform, ethylene dichloride, trichloroethylene, perchloroethylene, and o-dichlorobenzene (Battelle Memorial Institute, 1974). It should be emphasized that in any recovery strategy such as this, a residual will always be present, typically as a still bottom, and must receive adequate consideration for proper disposal.

Heavily Contaminated Wastes

In the case of heavily contaminated wastes, recovery of organic materials may be effected in a similar manner to that for lightly contaminated materials, especially in cases where there is a significant difference in boiling point between the desired material and the contaminants. While these potentials need to be evaluated on a case-by-case basis, several examples of promising recovery techniques have been reported.

In the wool industry, scouring and degreasing operations may result in a solvent heavily contaminated with lanolin and other greases. The solvent may be distilled and recycled within the plant; the still bottoms, consisting primarily of lanolin and grease, may also be recovered, if a satisfactory market is available (Booz Allen Research Inc., 1973).

In the petroleum industry, wastes from process condensate or steam stripper condensate or bottoms may be heavily contaminated with phenol. A proprietary solvent extraction process, the PHENEX process, has been proposed for recovery of phenol and removal of this material from the liquid stream (Booz Allen Research Inc., 1973).

In a number of industries, heavy ends or still bottoms are produced from distillation or other processes. Typically, in the organic chemical industries, liquids or semisolid wastes may result from the manufacturing process. Again, resource recovery from wastes of this nature may require a case-by-case analysis. However, two case studies from the literature are given to illustrate potential for resource recovery.

In the manufacture of chloromethane solvents, a waste stream is produced consisting of hexachlorobenzene, hexachlorobutadiene, and miscellaneous materials. An initial distillation of this waste yields a distillate which may be chlorinated at high temperature and pressure in a nickel tube to yield carbon tetrachloride. After quenching, and partial cooling and depressurization, the high boiling compounds may be distilled off and recycled back to the chlorine contactor. The remaining material may be separated into chlorine and carbon tetrachloride by distillation. The carbon tetrachloride may be further purified and marketed with the production from the main plant. Economics of this process indicate favorable costs, of about

1-2% of the total product value (Genser et al., 1977).

In the manufacture of perchloroethylene, a waste stream is produced which consists primarily of hexachlorobutadiene. By stripping the volatile material from this waste, recycling this to the main plant, and distillation of the remainder, hexachlorobutadiene can be produced. Including costs for land disposal of the still bottoms from the recovery operation, economic analysis indicates the potential for a net profit from the treatment/recovery operation (Genser et al., 1977).

Resource Recovery from Dilute Aqueous Solutions of Organics

There does not appear to be any significant potential in the near term for resource recovery from dilute aqueous solutions containing organic matter. The only possible exception to this statement may be in the case of highly specialized waste streams, such as those from the pharmaceutical industry, which might contain low concentrations of relatively valuable material. The major basis for this pessimism lies in the relatively high costs of probable separation processes which might be used to purify and concentrate the organic contaminants into a usable product.

The only possible recovery strategy for this group of wastes currently forseeable is the possible recovery of energy from this material when activated carbon is used in removal. In this case, during the thermal regeneration of carbon the process might be operated to provide a beneficial use of waste heat. It would not appear, however, from a cursory analysis, that this option will permit a net production, of energy in the GAC process.

Resource Recovery from Organic Solids

Although the major aims of hazardous waste disposal of organic solids are detoxification and volume reduction, opportunities exist for resource recovery. The general strategies used are energy recovery, direct recycling as a raw material in another industry or use of a pyrolytic system to generate liquid or gaseous fuels. Energy recovery from thermal processing is covered in a later section.

Contaminated organic solids (or liquids) which cannot be recycled must ultimately be diposed of by incineration. In some cases, recovery of the contaminate will result in a usable product. For example, hydrogen chloride is produced during incineration of chlorinated hydrocarbons. To meet air pollution regulations, this gas must be collected. Since hydrogen chloride or hydrochloric acid has economic value, its presence then becomes a credit rather than a liability (Novak, 1970; Ross, 1977; Santoleri, 1973).

Salts and Pure Organic Compounds

Although the volume of waste in this category is, in many locations, very small, salts and pure organic compounds are the best candidates for direct recycling (Tabakin *et al*., 1978). Wastes from one industry can sometimes be used directly as a raw material for another industry. This exchange can only take place when a mechanism exists for easy transfer. Hazardous waste clearinghouses provide this avenue for exchange (US EPA, 1976; Terry *et al*., 1976).

Tars and Residues

Tars and residues generally have little value for resource recovery other than their heat content. Energy recovery after thermal processing is possible if the heat content of the waste is high enough. However, with increased energy costs the fuel quality of residues has been steadily decreasing (Novak, 1970).

Sludges

Since most hazardous organic sludges commonly will require incineration, several possible methods of resource recovery might be feasible other than recovery.

Recovery of inorganic contaminants after incineration from the scrubber water or ash is possible. Metal oxides have some economic value, and can be recovered by extraction and ion exchange. These compounds can be reprocessed to recover the metals. Recovery of halogens from the scrubber water is another possible direction. For example, brominated tars and sludges, when incinerated, release free bromine. Recovery of the relatively valuable bromine, rather than its complete disposal, seems practicable (Novak, 1970; Sebastian, 1975; Folks et al., 1975; Santoleri, 1973; Ross, 1977; Hitchcock, 1979).

Resource Recovery from Organic Gases and Vapors

Organic gases and vapors will usually be incinerated or recycled at the point of production. Recycling is accomplished by solvent stripping, extraction or condensation. Tanked gases have the possibility of direct recycling as a raw material for another industry. Unwanted gases and organic vapors produced during disposal should be incinerated and can be used for energy recovery.

3.5 Energy Recovery

The recovery of energy and/or heating value from certain organic hazardous wastes is deserving of special consideration. In general, few incineration systems for toxic waste decomposition have been designed to recover energy since auxiliary fuel is almost always needed to ensure complete combustion with minimization of undesirable atmospheric emissions. However, knowledge of detailed feed composition and careful blending of wastes fed to an incinerator will reduce the auxiliary fuel needs, and thus reduce direct energy costs associated with incineration.

There are two basic manners in which energy recovery may be effected in thermal processing: heat recovery, and recovery of fuel value. Recovered heat may be used to preheat combustion air, or in steam generation for heat or power production. Heat exchangers are generally tubular, plate, or regenerative, and used for heat transfer between the exit gases of a combustion process and a working fluid. If air is the working fluid across a heat exchanger, it can be used as input to the combustion chamber to minimize fuel use. If the working fluid is water, the resulting steam or hot water may be sold or used in plant processes.

The second major type of energy recovery is utilization of the fuel value directly. Under pyrolytic conditions, a combustible liquid or gas may be produced from hazardous waste, which can be sold or used elsewhere (Novak, 1970; Ross, 1977; Boucher et al., 1977; Folks et al., 1975; Sebastian, 1975; Hitchcock, 1979). An interesting opportunity for conservation of the fuel value of hazardous waste is the utilization of these materials as feed for rotary kilns in cement manufacture. Test burns of chlorinated hazardous wastes at the St. Lawrence Cement facility in Ontario showed a 99.98 percent destruction of PCB's and a 99.99 percent destruction of chlorinated organics (US EPA, 1975). In this process, halogen gases are scrubbed into the cement product, and the fuel value of the hazardous waste directly reduces the need for fossil fuel inputs. A typical cement plant may require 10^{10} BTU of fuel per day, and initial indications suggest that substitution of up to 15 percent of this fuel value with chemical waste is possible (Alpha Portland Industries, personal communication). Certain industrials produce solvent laden air streams, which must normally be treated to control air emissions. One alternative to treatment and production of a solvent waste for disposal is to directly use the solvent laden air as the air feed to a boiler. The fuel value of the solvent is then recovered in the boiler.

In energy recovery from hazardous wastes, as in incineration of chemical wastes in general, the issues of materials deterioration remain relatively poorly understood. Operating problems such as corrosion, erosion, plugging, fouling, and refractory decomposition can decrease useful life of components. In addition, any utilization of energy in outside industries necessitates the production of a consistent amount of steam and/or fuel, and thus a relatively constant throughput of hazardous waste, both in terms of quality and quantity, must be maintained.

3.6 FACILITATION OF RECOVERY

Industrial materials are perceived as special or hazardous wastes requiring disposal when, in the judgment of the waste generator, there is insufficient economic value associated with the waste to warrant alternative modes of utilization. This judgment may be predicated upon institutional regulations, or upon a lack of awareness of a potential secondary industrial market for the material. Facilitation of recovery thus must consider both institutional options and strategies to encourage alternatives to ultimate disposal, and methods to identify secondary recovery and reuse markets. This latter aspect is usually addressed through waste exchangers and information clearinghouses.

Institutional Options. The National Conference of State Legislatures has recently completed a survey and analysis of state policy options to encourage alternatives to land disposal of hazardous wastes. This analysis identified several state options to encourage the use, reuse, reclamation, and recycling of hazardous waste. The states can encourage such alternatives to land disposal by providing financial, legal and institutional incentives and disincentives.

A variety of financial strategies have been described for encouraging alternative methods for management of hazardous waste. They include the use of fee structures, tax incentives and bonds. Fees can be structured to discourage undesirable disposal options such as land disposal, by making them higher for those generators who do not utilize use and reuse methods. They can encourage alternatives by setting lower fees for permits and licenses required of facilities that treat or recover hazardous waste. Tax incentives offer a positive inducement for business and industry to adopt alternative waste management methods. They include property and equipment tax exemptions, corporate income tax exemptions, accelerated depreciation schedules and sales, and use and excise tax exemptions for facilities which treat and recycle hazardous waste. Industrial revenue bonds may also be authorized to finance resource recovery facilities.

Illinois, for example, currently levies a uniform fee on all owners and operators of hazardous waste sites. Some other states structure fees to be higher for, or to be only levied on, those generators who do not utilize reuse and reduction methods.

Kansas authorizes its Department of Health and Environment, and Tennessee its Solid Waste Control Board, to establish a schedule of fees based on the degree of hazard and costs for treatment and disposal. In effect, these approaches allow the state to discourage high hazard waste disposal by scheduling higher fees for these facilities. Indiana places a tax of $1.50/ton on hazardous waste disposal, but it appears that this tax does not apply to resource recovery. In Ohio, those entities that detoxify or incinerate hazardous waste are not required to pay the fee which supports the state's special hazardous waste account. Such an approach places the financial burden on those facilities which would have the greatest tendency to call on the resources of the fund.

Recent Kentucky legislation authorizes the Department for Natural Resources and Environmental Protection to collect a tax. The annual hazardous waste management assessment is determined according to the quantity and volume of hazardous waste generated by the individual. The assessment for on-site treatment and disposal is one-half the amount for off-site treatment and disposal. On-site resource recovery and treatment facilities are exempt from any assessment unless the process involves the landfilling of hazardous waste. The legislative intent of the assessment is to reduce the amount of waste generated, promote alternatives to landfilling and encourage onsite as opposed to offsite management. The assessment on generators of waste destined for long-term containment without prior treatment is significantly higher than for generators of waste destined for treatment. This approach rewards those generators who provide pretreatment of their waste. In addition, the Department has developed a schedule of fees for the costs of processing applications for permits and exemptions that is lower for recyclers of hazardous waste. Maine's proposed three-tiered fee structure is similar to Kentucky's in that license fees, renewal fees and taxes on generators of hazardous waste will be lower for resource recovery activity.

Florida offers an alternative approach. Rather than raising the fees for generators who do not treat their waste, facilities which render waste non-hazardous are exempt from the four percent excise tax. The tax is "to be paid by each generator of hazardous waste in the state...for the privilege of generating hazardous waste." The tax is levied at four percent of the price of disposing, storing, or treating hazardous waste. Moreover, the tax is levied in addition to all other taxes imposed upon or paid by the generator. In addition to exemption treatment facilities which render the waste non-hazardous, the law exempts onsite generation and disposal. As in Kentucky, treatment and/or onsite facilities are encouraged. Along with money collected from permitting fees, fines, appropriations, etc., the money collected from the excise tax is used to support the state's Hazardous Waste Management Trust Fund. Table 3.1 is a summary of State fees on hazardous wastes disposal.

Similar to fee structures in that they may be used to encourage alternatives to land disposal, tax incentives offer a positive inducement to business and industry to adopt alternative waste management methods. While fees may be scheduled as a disincentive to landfilling, taxes can be structured to reward those businesses and industries that engage in treatment or recovery of hazardous waste.

There are several types of tax incentives that can be applied specifically to hazardous waste treatment. Tax incentives provided for solid waste facilities or pollution control equipment may also be applied to hazardous waste management with amendment of statutory language. The range of tax incentives includes property tax exemptions, "breaks" on equipment taxes, corporate income tax exemptions, and sales, use and excise tax exemptions. An amendment (S.169) to the Federal Internal Revenue Code, and intended to provide tax-exempt financing for process changes which prevent the creation of pollution (e.g. source reduction and resource recovery) was introduced in the 97th Congress (Congressional Record 1981). This proposed amendment specifically cites examples of pollution prevention and resource recovery to be covered under the amended Code.

Although almost all states authorize the issuance of industrial revenue

Table 3.1 Summary of Selected State Hazardous Waste Disposal Fees (Bulanowski, *et al.*, 1981).

State	Volume Basis	Fee, $
Alabama	gallon	0.036
	ton	5.00
Florida	see Footnote (1)	****
Illinois	gallon	0.01
	cubic yard	2.02
Indiana	ton	1.50
Iowa	see Footnote (2)	****
Kansas	cubic yard	0.25
Kentucky	gallon (1981)	0.02
	gallon (1983)	0.05
Maine	gallon (on-site)	0.12
	(off-site)	0.15
Missouri	see Footnote (3)	****
New Jersey	see Footnote (4)	****
Ohio	see Footnote (5)	****

(1) 4 percent tax on charge for disposing of waste
(2) 2 percent surcharge tax
(3) 2 percent tax on gross charges and fees
(4) 5 percent tax on gross receipts of disposal facility
(5) 4 percent tax on gross charges

bonds, only five states specifically address their use in resource recovery. These states are North Carolina, Florida, Illinois, Mississippi, and Georgia. In Illinois, facilities for which such funds are available include those engaged in "reducing, controlling or preventing pollution...(or those that) reduce the volume or composition of hazardous waste by changing or replacing manufacturing equipment or processes...recycle hazardous waste, or recover resources from hazardous waste."

Legal and institutional policies available to encourage land disposal alternatives range from legislative and regulatory incentives and disincentives to the establishment of state research and development programs. In Illinois, a portion of the State hazardous waste disposal fee is allocated under the enabling legislation to a research and development fund. Legal options consist of excluding recycled and reused materials from regulatory programs; eliminating permit requirements for resource recovery facilities or on-site hazardous waste systems; expediting and the permitting process (i.e. fast-track permitting) for recycling facilities; restricting the burial of certain hazardous waste when it is feasible that it be treated or recycled; and lessening the liability standards for alternative management technologies.

There are many approaches to land disposal restrictions. Perhaps the strongest position that can be taken is an outright ban on land burial. New York's Department of Environmental Conservation has announced that they are currently writing regulations to "ban landfilling of environmentally persistent and highly mobile chemical wastes..." Further, New York has denied permits on the grounds that they failed to adequately provide for technologies that offer alternatives to land burial. Another approach to banning land disposal of hazardous waste is to require neutralization, detoxification, solidification or encapsulation of the waste prior to land disposal.

Effective January, 1983, the State of California will ban the land disposal of six categories of hazardous wastes which, together, represent about 40 percent of all hazardous wastes which otherwise would be deposited in landfills. The banned wastes consist of polychlorinated biphenyls, pesticides, toxic metals, cyanides, halogenated organics, and non-halogenated volatile organics. The current volume of these wastes landfilled in California is 500,000 tons/year. The intent of the ban is to force the wastes to be recycled, detoxified, or destroyed, as alternatives to land disposal.

In Illinois a petition has been filed by a citizen's group with the Illinois Pollution Control Board, requesting that the Board promulgate a regulation prohibiting the disposal of the class of compounds termed "chlorinated solvents" in landfills, as well as the sludges and still bottoms from the recovery of these solvents. In addition, the Illinois Environmental Protection Act was recently amended to require the IEPA (effective January 1, 1987) to permit hazardous waste disposal to a landfill only after the waste stream generator has demonstrated to the IEPA that,..."considering technological feasibility and economic reasonableness, the waste cannot be reasonably recycled for reuse, incinerated or chemically, physically or biologically treated so as to neutralize the waste and render it non-hazardous."

To make this strategy of land disposal restrictions more workable for the regulated community, some states such as Illinois specifically require that it must be technically feasible and economically reasonable to require recycling or treatment. The state statutes that require this, often authorize the agency to describe in rules and regulations what is technically or economically feasible and what wastes should be restricted from landfills.

The institutional strategies designed to encourage alternatives to land disposal include establishment of government operated waste exchanges, research and development programs, and state ownership of alternative technology facilities. Waste exchanges direct material that would otherwise enter the waste stream to a beneficial use or reuse; they lower disposal costs and conserve raw materials and energy necessary to process virgin materials. Research and development can advance the implementation of alternative resource recovery technologies through direct state research or technical assistance programs. Perhaps the most effective institutional strategy is the establishment of state-owned facilities that provide alternative technologies; this permits the regulatory agency to set specific treatment and recycling requirements on the hazardous wastes which will be handled by the facility.

Waste Exchanges. In resource recovery of hazardous wastes it is important to recognize that the generator of a given stream may not necessarily recognize the potential for recovery by an industry outside of its immediate scope of production. The process of secondary recovery can be facilitated by the establishment of waste exchanges.

Waste exchanges are institutions which promote waste reuse by one of two methods. Most waste exchanges act as information clearinghouses, by collecting information on materials to be disposed and potential buyers (or recipients) of such waste. Other waste exchanges act by accepting (or purchasing) wastes from a generator for sale to a user. In the case of a waste materials exchange the acceptance and sale may be merely a paper transaction, as in the case of a brokerage, rather than a physical acceptance and transfer.

The earliest waste exchanges were established in Western Europe, beginning in 1972. These European organizations now typically have a 30-40 percent success rate in exchanging materials contained in their listing. The U.S. waste exchange industry has developed more recently, and its success rate is only about 10 percent. A comprehensive review of foreign and U.S. background and experience in waste exchange has recently been published.

Constraints on successful waste exchange include long transport distance between the generation and reuse points, and cost of waste purification prior to reuse. Factors which enhance waste exchange include the inherent value of the material, high concentration and purity, quantity and reliability of availability, and high offsetting costs for ultimate disposal.

Due to transportation cost factors, most waste exchanges operate on a local, state or regional basis. Of the top ten states in terms of volumes of hazardous wastes generated, four (Illinois, Indiana, Michigan and Ohio) are located in the midwest, as are seven of the 28 known Waste Exchanges.

Waste exchanges may be operated by government bodies (e.g., Illinois, New York), trade associations such as State Chambers of Commerce, individual industrial companies to handle their specific wastes, or as private, profit oriented ventures. This latter approach appears most successful, due to both confidentiality aspects and aggressive marketing techniques. Confidentiality is often of industry concern, for two reasons;

1) to avoid alerting competitors to proprietary information which is perceived to give the generator an economic edge, and
2) industry may feel that despite good intentions, a regulatory body may use "inside information" against the generator.

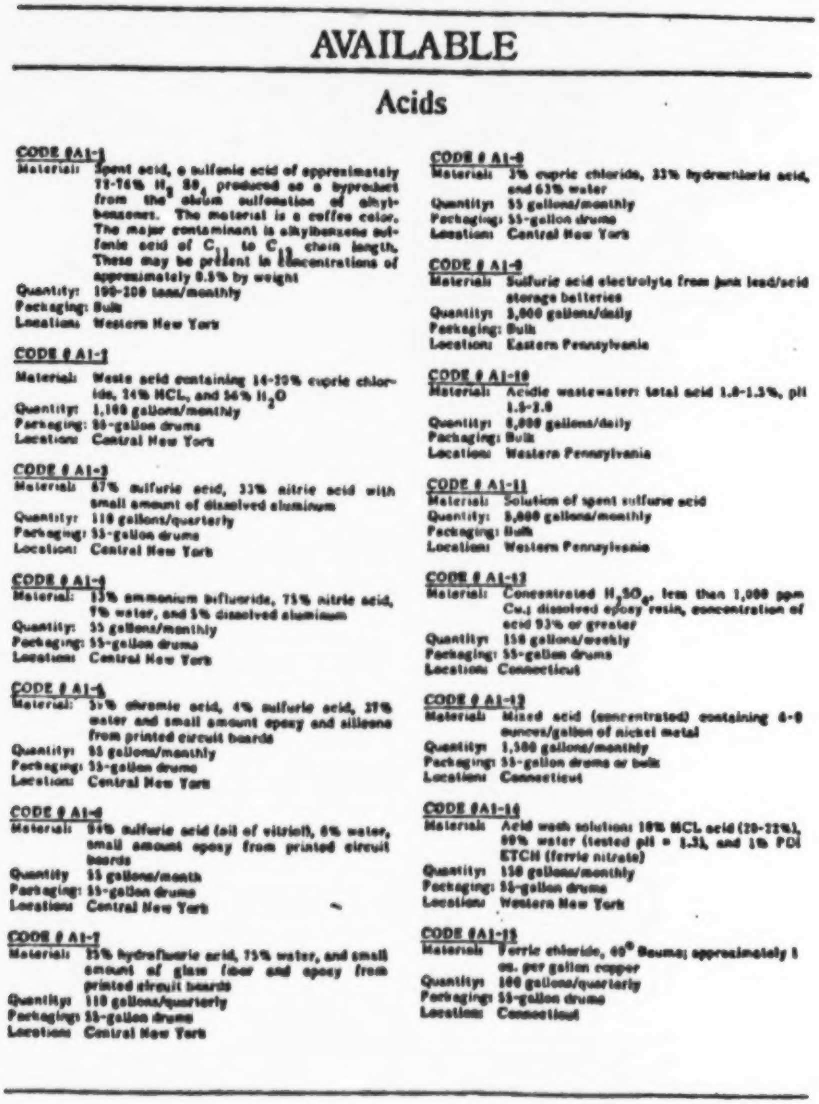
Some waste exchanges offer the opportunity for the generator to approve a proposed user in a waste exchange activity.

The general categories of wastes which have been successfully exchanged to date in the U.S. include concentrated acids, alkalis, solvents, catalysts, oils, other combustibles (for fuel value), and wastes with high concentration of metals. Other, more specialized materials have also been successfully exchanged. Examples include gypsum wallboard (used as a soil conditioner), scrap roofing shingles and trimmings, and calcium hypochlorite. However, solvents and waste oils appear to be the most highly sought materials for waste exchange. An example listing from a waste exchange bulletin is presented in Table 3.3. Such bulletins normally list both materials available and materials sought. Although on an industry-wide basis it has been estimated that with available technology only about 3 percent (6 million metric tons/year) of the total U.S. hazardous wastes volume generated has potential for waste exchange, the percentage in selected industrial categories is much higher (Table 3.2). In general, waste exchanges take place from larger companies using continuous manufacturing processes to smaller companies using batch processes; from basic chemical manufacturers to formulator; and from industries with high purity requirements (e.g. pharmaceuticals) to those with low purity requirements (e.g. paints).

Table 3.2 Categories of Industry Producing Hazardous Wastes With Significant Potential for Waste Exchange and Reuse (USEPA, 1977)

Industry Category	SIC Code	Estimated Percent With Reuse Potential
Pharmaceuticals	2831, 2833	95
Paints and Allied Products	285x	40
Organic Chemicals	2865, 2869	25
Petroleum Refining	2911	10
Small Industrial Machinery	355x	20

Table 3.3 Partial Example Listing from a Waste Exchange Bulletin



AVAILABLE

Acids

CODE #A1-1
Material: Spent acid, a sulfonic acid of approximately 72-76% H_2SO_4 produced as a byproduct from the oleum sulfonation of alkylbenzenes. The material is a coffee color. The major contaminant is alkylbenzene sulfonic acid of C_{11} to C_{13} chain length. These may be present in concentrations of approximately 0.5% by weight
Quantity: 190-200 tons/monthly
Packaging: Bulk
Location: Western New York

CODE # A1-2
Material: Waste acid containing 14-20% cupric chloride, 24% HCL, and 56% H_2O
Quantity: 1,100 gallons/monthly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-3
Material: 67% sulfuric acid, 33% nitric acid with small amount of dissolved aluminum
Quantity: 110 gallons/quarterly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-4
Material: 13% ammonium bifluoride, 73% nitric acid, 9% water, and 5% dissolved aluminum
Quantity: 55 gallons/monthly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-5
Material: 57% chromic acid, 4% sulfuric acid, 37% water and small amount epoxy and silicone from printed circuit boards
Quantity: 55 gallons/monthly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-6
Material: 94% sulfuric acid (oil of vitriol), 6% water, small amount epoxy from printed circuit boards
Quantity 55 gallons/month
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-7
Material: 25% hydrofluoric acid, 75% water, and small amount of glass fiber and epoxy from printed circuit boards
Quantity: 110 gallons/quarterly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-8
Material: 3% cupric chloride, 33% hydrochloric acid, and 63% water
Quantity: 55 gallons/monthly
Packaging: 55-gallon drums
Location: Central New York

CODE # A1-9
Material: Sulfuric acid electrolyte from junk lead/acid storage batteries
Quantity: 3,000 gallons/daily
Packaging: Bulk
Location: Eastern Pennsylvania

CODE # A1-10
Material: Acidic wastewater: total acid 1.0-1.5%, pH 1.5-2.0
Quantity: 8,000 gallons/daily
Packaging: Bulk
Location: Western Pennsylvania

CODE # A1-11
Material: Solution of spent sulfuric acid
Quantity: 5,000 gallons/monthly
Packaging: Bulk
Location: Western Pennsylvania

CODE # A1-12
Material: Concentrated H_2SO_4, less than 1,000 ppm Cu.; dissolved epoxy resin, concentration of acid 93% or greater
Quantity: 150 gallons/weekly
Packaging: 55-gallon drums
Location: Connecticut

CODE # A1-13
Material: Mixed acid (concentrated) containing 6-8 ounces/gallon of nickel metal
Quantity: 1,500 gallons/monthly
Packaging: 55-gallon drums or bulk
Location: Connecticut

CODE #A1-14
Material: Acid wash solution: 10% HCL acid (20-22%), 89% water (tested pH = 1.3), and 1% PDI ETCH (ferric nitrate)
Quantity: 150 gallons/monthly
Packaging: 55-gallon drums
Location: Western New York

CODE #A1-15
Material: Ferric chloride, 40° Baume; approximately 1 oz. per gallon copper
Quantity: 100 gallons/quarterly
Packaging: 55-gallon drums
Location: Connecticut

3.7 CONCLUSIONS

The potential recovery strategies for the various classes of wastes are summarized in Tables 3.4 and 3.5. The areas having the greatest potential for recovery are:

- energy recovery from concentrated organic liquid wastes, e.g., incineration of waste organic liquids and oils
- recovery of materials from concentrated organic liquid wastes, e.g., distillation and recovery of waste solvents
- recovery of metals from industrial sludges and metal plating wastes, e.g., recovery of chromium, copper and nickel from spent plating baths

It appears that the following techniques also have potential for development and should be investigated further for possible application for material and energy recovery:

- use of flue gases for pollution control purposes, e.g. neutralization of alkaline wastes
- use of cement kilns for simultaneous destruction of halogenated organic liquids, and energy recovery
- recovery of metal oxides from incinerator ash and other solids
- use of heat exchangers and waste heat boilers for heat recovery
- minimization of auxiliary fuel by mixing wastes of high and low heating value
- use of pyrolysis for fuel recovery and ash fusion prevention
- the development of a waste exchange program

Two typical processing schemes for material and energy recovery are illustrated in Figures 3.1 and 3.2.

Detailed design and analysis of resource recovery facilities are directly dependent on the specific nature, volume and composition of the waste to be treated. Economic feasibility of resource recovery is highly sensitive to such factors as value of recovered products, transportation and storage costs. Transportation and storage at a recovery facility may involve special risks not present at facilities primarily designed for disposal.

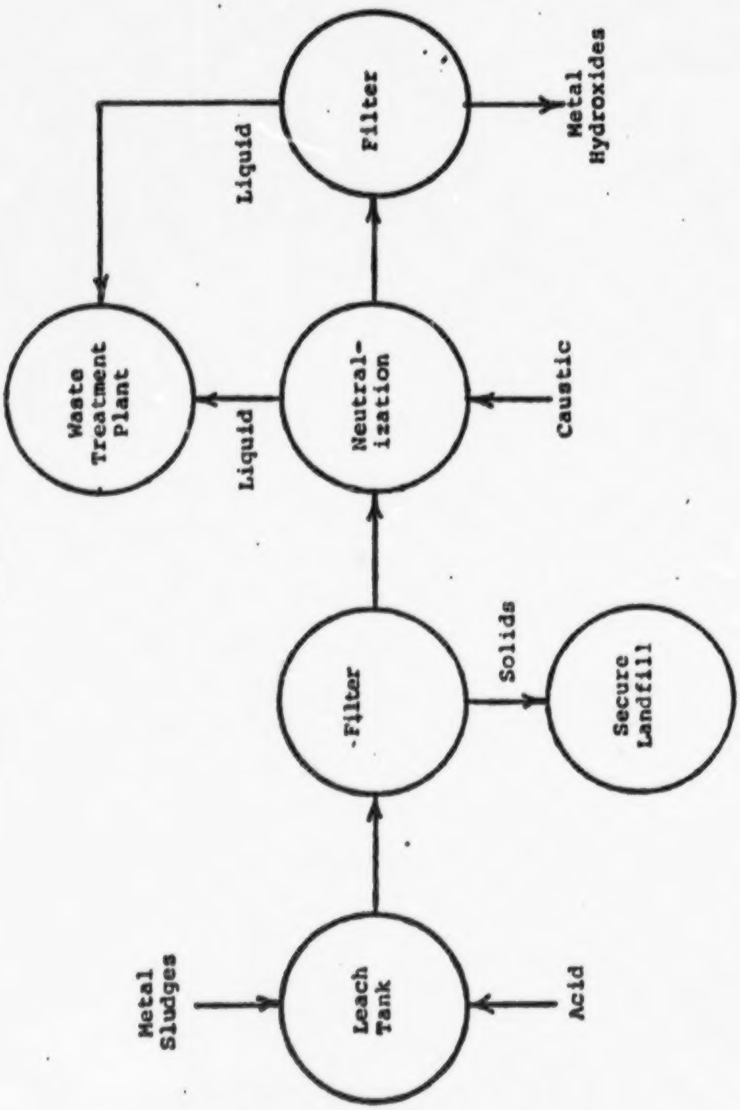

Metal Sludges
Leach Tank
Acid
Filter
Solids
Secure Landfill
Neutral-ization
Caustic
Liquid
Waste Treatment Plant
Liquid
Filter
Metal Hydroxides

Figure 3.1
Recovery of Metals from Sludges
(Source: Shuster *et al.*, 1979)

Figure 3.2
Recovery of Material & Energy from Waste Solvents
(Source: Shuster et al., 1979)

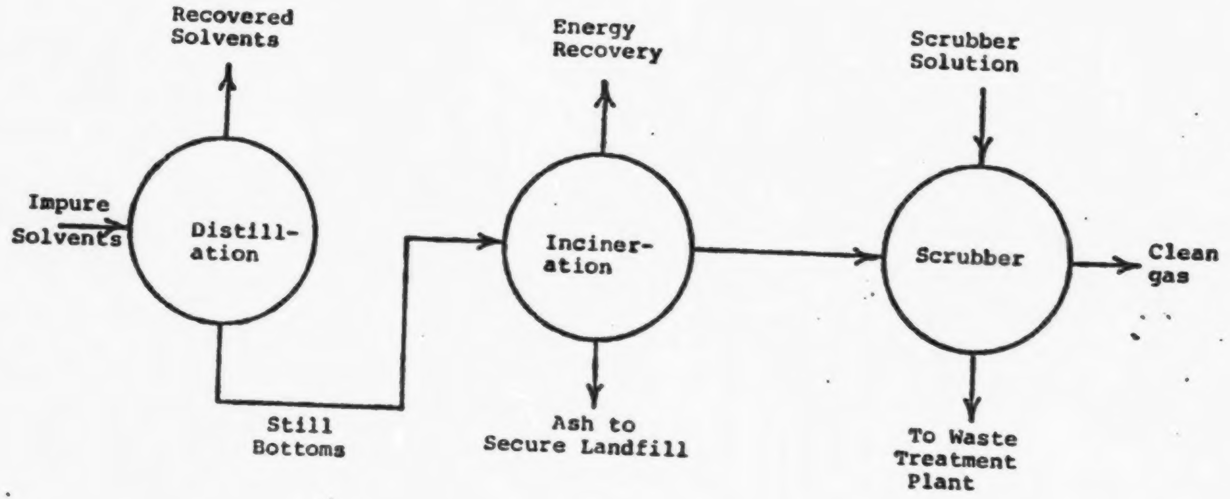

Impure Solvents
Distillation
Recovered Solvents
Still Bottoms
Incineration
Energy Recovery
Ash to Secure Landfill
Scrubber Solution
Scrubber
Clean gas
To Waste Treatment Plant

Table 3.4

Summary of Resource & Energy Recovery Potential for Hazardous Wastes (Inorganic) (Source: Shuster *et al*., 1979)

Type of Waste	Direct recovery or reuse	Raw material for secondary use	Energy recovery	Use in pollution control	Low potential for recovery
101-Acid Soln. - no contamin.	x	x		x	
102-Acid Soln. - with metals					
Heavy metals (except Cr)	x	x			
Chromium	x				
Noble metals	x				
Pickle liquor	x	x		x	
103-Acid soln. - with org.					
Emulsified org.		x	x		
Dissolved org.	x	x			
104-Acid sludges					
Inert solids					x
Solids with metals	x				
Organic solids					x
105-Acid gases				x	
111-Alk. soln. - with metals	x	x		x	
112-Alk. soln. - with org.	x	x	x		
113-Cyanide soln.					x
114-Cleaning soln.					x
115-Alkaline sludges					
Inert solids					x
Solids with metals	x				
Organic solids					x
121-Salt solutions					x
122-Solids					x
123-Metals					
Heavy metals	x				
Alkali metals					x
Volatile metals	x	x			
124-Non-metals					
Phos. sulf. compds.	x				
Asbestos					x

Table 3.5
Summary of Resources & Energy Recovery Potential
for Hazardous Wastes (Organic)
(Source: Shuster et al., 1979)

Types of Waste	Direct recovery or reuse	Raw material for secondary use	Energy recovery	Use in pollution control	Low potential for recovery
Concentrated Liquids					
201-Clean, halogenated	x	x	x		
202-Clean, non-halogenated	x	x	x		
203-Clean, solvent mixtures	x	x	x		
204-Dirty, halogenated	x	x	x		
205-Dirty, non-halogenated	x	x	x		
206-Dirty, solvent mixtures	x	x	x		
Dilute Aqueous Solutions					
211-Readily oxidized, halog.					x
212-Readily oxidized, non-halog.					x
213-Difficult to oxid., halog.					x
214-Difficult to oxid., non-halog.					x
Organic Solids					
221-Salts and other solids	x	x			
222-Tars and residues			x		
223-Sludges	x		x		
Organic Gases/Vapors					
231-Combustible			x		
Special Wastes					
311-Strong oxidizing agents					
312-Explosives					
313-Biological wastes					x

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CHAPTER 4

SECTION 1

DEVELOPING TECHNOLOGY FOR RECOVERY, REUSE, OR RECYCLE

Supercritical Fluid Extraction

Supercritical fluid extraction is a recently recognized separation technique which has received much attention (Chem. Eng., 1979). Although conditions vary for a given application, the supercritical fluid extraction process has two fundamental operations. In the first step, the fluid, usually at a pressure of 4,000-5,000 psi, and a density comparable to liquid hexane, flows through the material to be treated in an extraction vessel. At this elevated pressure its solvation power is greatly enhanced, and the fluid becomes solute-laden. The fluid is then depressurized in a separation tank. Because the solvation power of a supercritically compressed fluid varies with respect to pressure, some of the extract will drop out of solution. Little solvent residue is generally left behind in the extract.

According to the manufacturer, the process can extract materials such as oils from natural products, organic pollutants from wastewater, aromatic isomers from mixtures, low-molecular weight materials from polymers, and light components from coal (Chem. Eng., 1982). It has also been applied to the regeneration of wastewater adsorption beds (Eckert). Among the solvents which can be used in the system are carbon dioxide, water, oxygen, ethlyene, propane, and propylene (Chem. Eng., 1982).

Actual separation pressures, which can range from 500 to 3,000 psi, depend on the economics of the application. Because a greater pressure change requires more energy than a small one, a tradeoff exists between the benefit of total solute recovery by depressurization to ambient conditions and the cost of repressurizing the solvent for another pass through the system (Chem. Eng., 1982).

Electrolytic Demulsification

In the future, physical separation techniques will be required which have capabilitites surpassing those of conventional technology for separating intimate liquid-liquid and liquid-gas mixtures (EPA, 1979). In several large-scale industrial processes, the liquid-liquid mixtures occur in the form of micro-emulsions of organic liquids in aqueous solutions. The treatment of these emulsions by conventional means would require large batch operations and generate voluminous quantities of sludge from which recovery is uneconomical. There have recently been some promising developments in the area of emulsion-breaking.

It has been shown that passing the micro-emulsion through a packed-bed anode of iron (or low-carbon steel) chips in which ferrous ions are electrochemically generated is an extremely effective destabilization technique. The process requires simultaneous oxygenation by sparging or by electrolytic evolution from a carbon anode (Weintraub and Gealer, 1977 and Weintraub, Dzriechiuch, and Gealer, 1976). Such a process would have application in the treatment of oily wastewater streams generated by the use of cutting oils in industrial matching operations (Gealer, Golavou, and Weintraub). Other possible applications include tertiary oil recovery, where alkali and surfactants are injected into wells and metal recovery from low-grade mineral resources (Tavlarides, 1981), where solvent extraction is used as a concentration device or as a pollution control step.

The mechanism by which the destabilization of micro-emulsions occurs in the electrolyte process is only partially understood (Dziecimuch, Weintraub and Gealer, 1976), although the incentive for more research into the development of a continuous process for the treatment of oil-in-water emulsions exists. The process should have as a primary requirement not only that it is effective in destabilizing micro-emulsions but also that the sludge it generates should be as "dry" as possible to facilitate recovery of organics. (IWERC Report, 1981).

Liquid Surfactant Membranes

Liquid membranes are formed when an emulsion of two immiscible phases is dispersed in a third (continuous) phase. The encapsulated phase of the emulsion is thus set apart from the continuous phase by the second phase of the emulsion, which is immiscible with either the encapsulated or continuous phases and constitutes, within this context, the liquid membrane. The stability of the emulsion is maintained by the addition of surfactants and stabilizing agents.

When developed for a given application, the three-phase system may be used to facilitate separation of components in a mixture by selective diffusion of the desired component from the continuous phase to the encapsulated phase or vice versa. Following this transfer, the three phases can be separated by first settling and separating the emulsion and the continuous phase, and then breaking the emulsion (Wasan, 1982).

Liquid surfactant membranes have been shown to be of use in recovering phenol, ammonia, organic acids, amines, and hydrogen sulfide from wastewater (Cahn and Li, 1974; Cahn, Li, and Miday, 1978; and Li, Cahn, and Shrier, 1973). The separation of inorganic ions such as chromium and copper from solution has also been studied (Hochhanser, 1975; Strzelbicki and Charewica; and Senkan and Stauffer, 1981). Use of this technology is curbed by a lack of information pertaining to mechanisms which can be used to maximize flux into and capacity within the receiving phase, and an understanding of the relative impact of process variables on these mechanisms (Wasan, 1982).

Solidification/Encapsulation

The process of solidification and encapsulation involve the deactivation and immobilization of a liquid or semi-solid (such as a sludge by converting it to an inert mass suitable for landfill disposal (Senkan and Stauffer, 1981 and Patterson and Haas, 1982). For hazardous wastes which cannot be otherwise detoxified or incinerated, these processes are the only environmentally sound method of preparation for storage, and therefore promise to again rank among the most important disposal techniques (Senkan and Stauffer, 1981). Encapsulation is a process in which a liquid is encased and entrapped by an impermeable coat, such as polyethylene or polybutadiene. In solidification, a gelling agent such as cement or lime is added which chemically reacts with the waste to form an impermeable mass. Several technologies exist for these processes (Patterson and Haas, 1982).

The major wastes currently treated by solidification and encapsulation processes are toxic and soluble inorganics and stack-gas-scrubber sludges (Pojasek, 1979). While short-term leaching studies indicate that the materials produced by the processes may be stable, little information is available on their stability during the contact with leachate or water over long periods of time (Patterson and Haas, 1982).

The solidification/encapsulation technologies currently in use are not compatible with all wastes. Organics and strong oxidants are incompatible with the majority of these technologies, although toxic anions and acidic materials in a waste may also be cause for its incompatibility with a given process (Pojasek, 1979). In some cases, the mass which results following treatment is flammable or may deteriorate upon contact with organic solvents (Senkan and Stauffer, 1981). Due to the disadvantages associated with currently available technologies, the development of improved methods is desirable.

Dissolution

Dissolution may be defined as the complete or partial transfer of one or more components from a solid phase into a liquid phase in contact with the solid. The reaction involves some degree of chemical transformation (solvation, ionization, oxidation) of the species being dissolved (Noyes Data Corp., 1978). Although dissolution reactions are used in nearly all areas of chemical processing, there has been recent interest in the in-situ dissolution of uranium (Tavlarides) from ore and of bitumen from tar sands (Shahinpoor, 1982).

In the case of in-site leaching of uranium from underground deposits, the subsurface deposit is flooded with leach solution and then pumped to the surface ready for uranium recovery. Advantages of this method are a significant reduction of processing costs and minimal disturbance to the surface conditions, as well as production of a relatively small volume of waste requiring disposal (Tavlarides, 1983).

The goal of in-situ bitumen recovery is to reduce the viscosity of the bitumen while it is in place, by heating and/or diluting it, and to subsequently collect the liquefied product. Several solvents capable of reducing oil viscosity are available, although they are generally more expensive than the oil produced. Economic success therefore requires a high percentage of solvent recovery, which is often difficult to achieve. In certain cases, water may be a suitable solvent (Shahinpoor, 1982)

The in-situ dissolution of uranium is feasible only where the ore body is contained within a rock formation which is relatively impermeable. Groundwater contamination may otherwise be a problem (Tavlarides). Potential environmental impacts of producing oil from tar sands appear, on the basis of methods tested to date, to be similar to those of conventional oil field operations (Shahinpoor, 1982).

Particle Conditioning

In the presence of water, solids have an intrinsic electrical surface charge. Almost all matter dispersed in spent process water such as oil particles, salt, biocolloids, inorganic colloids, etc., has a negative charge which is repelled by the negative electrical surface charge of granular media. In order to maximize filtration efficiency, these coulombic repulsive forces must be regulated through control of the physicochemical properties of the dispersed solids. The colloids must be destabilized into agglomerates tough enough to resist redispersive hydraulic forces in the filter.

Historically, granular media filtration has been viewed as a polishing step following a clarifier. More recently, direct filtration of highly contaminated has been investigated. Results indicate a large savings in capital, chemical, and sludge treatment costs may be realized. Charge neutralization or reversal by adsorption of a destabilizing chemical to the colloid is a key mechanism for optimization of direct filtration. When molecules of the added chemical attach to two or more colloids, aggregation and bridging occurs, and agglomerates are formed which resist redispersion.

The processes are demonstrated in the case of removal of coke fines from hydraulic decoking water. Coke fines are originally stabilized by negative zeta potential. This charge is easily reversed by the addition of cationic polyelectrolytes. The polyelectrolytes, which also have good bridging properties, cause most of the solids to be enmeshed in a polymer. Upon addition of a small amount of weakly anionic polyelectrolyte, the positively charged particles are "collected" into massive, easily separable aggregates. Once the aggregates are formed, the forces which bind them are strong enough to resist redispersion by the hydraulic forces of direct filtration (Grutsch and Mallott, 1977).

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CHAPTER 5

SECTION II

SORPTION

5.1 INTRODUCTION

According to Geankoplis (1978), there are presently many chemical process materials and biological substances that occur as mixtures of different components in the gas, liquid or solid phase. If it is desired to remove one or more of these components from its original phase, another phase must be contacted.

The term sorption includes both adsorption and absorption and refers to a process in which a solute(s) (mixture component) moves from one phase and is accumulated in another. Adsorption occurs when material is collected at the interface between two phases. Adsorption can occur between a liquid-liquid, gas-liquid or liquid-solid interface (Weber, 1972). In absorption, the two phases are brought into contact such that the mixture components can diffuse from one phase to another, during the contact of the two phases, the components of the original mixture redistribute themselves between the phases. The following chapter is divided into the following sections:

1. Absorption
2. Adsorption of Inorganic and Organics
3. Adsorption of Gases

5.2 ABSORPTION

The absorption of gases in liquids is one of the most frequently used techniques for controlling the composition of industrial waste gases prior to their discharge to the atmosphere. Waste gases are generally a mixture of gaseous components, some of which are soluble in a selected liquid phase. Direct contact of gas with liquid enables mass transfer to take place between the phases in directions governed basically by the concentration gradients of the individual components.

The rates of mass transfer between the gas and adsorbent are determined mainly by the amount of surface area available for absorption. Other factors governing the rate of absorption, such as the solubility of the gas in the absorbent and the degree of chemical reaction, are characteristic of the constituents involved and independent of the equipment used. (U.S. EPA, 1978).

Mass transfer between two fluids is carried out by eddy diffusion in the bulk of each phase and by molecular diffusion close to the interphase boundary. It is assumed that complete equilibrium is established instantaneously at the boundary, and that from this boundary, active species are transported deeper into each phase by molecular diffusion followed at some depth by mixing of isolated elements caused by eddy currents in the bulk phase. Eddy diffusion is orders of magnitude faster than molecular diffusion. The overall mass transfer rate is therefore controlled by mass fluxes within the molecular diffusion layers.

Using several basic assumptions, two mathematical models have been developed. The simpler theory is based on the assumption that molecular diffusion in both phases is predominantly in thin layers with laminar flow conditions in which the concentration gradient is invariable with time. Lewis and Whitman, adopting these steady state assumptions in both laminar layers, developed a two film theory.

Since in many cases the concept of laminar steady flow cannot represent the true nature of the process, the conditions of unsteady molecular diffusion have been incorporated into more advanced models. It is assumed that an element of liquid stays in contact with the gas at an interphase boundary for a limited time. After this, it is transported by eddy currents into the bulk of the phase and replaced by another element initially with a uniform concentration distribution. During the contact period, active species diffuse into an element developing a concentration gradient which changes both with time and position. (Bettelheim, et al. 1978).

In most cases, absorption of one component is simultaneously accompanied by the desorption of another. Deliberate desorption can be achieved by a change of physical conditions, stripping of the liquid with inert gas (or steam), or by chemical decomposition of the sorbent. Absorption followed by desorption constitutes a cyclic operation which allows reuse of the sorbent and acts as a device for separation and concentration of the selected gas. (Bettelheim, et al. 1978).

Gas absorption equipment is designed to provide thorough contact between the gas and liquid solvent to permit interphase diffusion of the materials. Contact may be provided by various types of equipment, the most common being plate and packed towers.

Plate towers employ stepwise contact. Several plates or trays are arranged such that gas is dispersed through a layer of liquid on each plate. The number of plates required is dictated by the difficulty of the mass transfer operation and the desired degree of absorption.

Packed towers are filled with a packing material having a large surface to volume ratio. The packing is wetted by the absorbent, providing a large liquid film surface area for continuous contact with the gas.

The flow through plate and packed towers is usually countercurrent, with the liquid being introduced at the top and the gas at the bottom. This arrangement results in the highest possible transfer efficiency.

Spray towers and venturi scrubbers have more limited application to gas absorption. Spray towers dispense liquid absorbent in a spray through which the gas is sent, while venturi scrubbers contact the gas and the absorbent in the throat of a venturi nozzle. The gas-liquid mixture then enters an entrainment separator in which centrifugal force separates the liquid droplets from the gas.

Packed and spray towers introduce lower pressure losses than do plate towers, and there is a high pressure drop associated with the operating velocities of the venturi scrubber. Power requirements for venturi scrubber operation are consequently large. Although spray towers have the advantage of removing particular matter without plugging, they provide the least effective mass transfer capability and their use is restricted to applications requiring only limited removal of highly soluble gases. Venturi scrubbers, also highly efficient for particulate removal, are preferred for removal of a highly soluble gas from a dirty gas stream.

Because spray towers and venturi scrubbers have limited application to absorption, packed or plate towers are usually the equipment of choice. A comparison of these two types of equipment is given in Table 5.1. (U.S. EPA, 1978).

TABLE 5.1 COMPARISON OF PACKED AND PLATE TOWERS (U.S. EPA, 1978)

1. Packed towers are less expensive than plate towers when materials of construction must be corrosion resistant.

2. Packed towers have smaller pressure drops than plate towers designed for the same throughput.

3. Packed towers are preferred for foamy liquids.

4. Packed towers usually have a smaller liquid holdup than plate towers.

5. Plate towers are preferred when the liquid contains suspended solids since plate towers are more easily cleaned.

6. Plate towers are preferred for larger installations because they minimize channeling and reduce tower height.

7. Plate towers are more suitable when the process involves appreciable temperature variation, since expansions and contractions due to temperature changes may crush the tower packing.

8. Plate towers are preferred when heat must be removed, because cooling coils are more easily installed.

9. Packed towers are preferred in sizes up to 2 feet in diameter if other conditions are nearly equal.

5.2.1 Limiting Technology

In general, absorption is most efficient under the following conditions:

1. The vapors to be absorbed are quite soluble in the absorbent.
2. The absorbent is relatively nonvolatile.
3. The absorbent is noncorrosive.
4. The absorbent has low viscosity.
5. The solvent is nontoxic, nonflammable, chemically stable, and has a low freezing point.

The rate of mass transfer between the absorbent and the gas is dependent on the amount of surface area available for absorption. The solubility of the gas in the absorbent and the degree of chemical reaction which takes place are characteristics of the constituents involved. Gas absorption equipment must be designed to provide adequate contact between the gas and absorbent liquid to permit interphase diffusion of the organic vapors (U.S. EPA, May 1978).

Selection of a suitable liquid solvent and the determination of the limits of absorption efficiency are based on solubility data. In most cases, no formula is available for calculation of the solubility and only tabulated or graphical data can be used.

5.2.2 Recycle, Reuse, Recovery Applications: Organics

Many industrial processes which employ phenol or phenolic resins are faced with the problem of toxicity and odor problems arising from the evolution of phenol and phenol-derived volatile substances into the air. A method developed for substantially reducing this atmospheric contamination consists of absorbing the contaminants in an aqueous solution of a water soluble phenol-formaldehyde resin and then condensing the mixture of absorbing resin and absorbed contaminants to form an augmented resin by-product (Baker, 1975).

Gases contaminated with vapors from volatile organic liquids may be recovered by contacting the vapor-containing gas with an absorbent sponge oil in an absorbing tower. The sponge oil, rich in absorbed vapors, is conveyed to a flash tank wherein the absorbed vapors are removed and recovered. Following this process, the sponge oil can be successfully reused (Haines, 1975).

Nichols (1973) describes a low-temperature recirculating absorption system capable of 90% hydrocarbon recovery and designed to recover vapors present in saturated vapor air mixtures from the loading and storing installations of oil companies. The system consists of an absorber and components which condition the vapors and liquid, improve absorption efficiency, reduce thermal losses, and/or improve system safety. In the system, incoming vent gases are saturated with fuel and the entrained liquid is allowed to settle out before passing to an air compressor. The gases are brought to 45 psig and approximately 300°F as they pass from saturator to compressor. They then proceed to an aftercooler where temperature is reduced to an ambient level. From the aftercooler, they pass through a bubble bar and into an absorber where they are absorbed by sprayed gasoline.

5.2.3 Recycle, Reuse, Recovery Applications: Inorganics

When plastic wastes are burned in an incinerator, they tend to exhaust a dark smoke resulting from incomplete combustion. In the case of polyvinyl chloride (pvc) incineration, serious corrosion of equipment as well as air pollution by hydrogen chloride gas will occur. Oda, et al. (1975) devised a disposal system which results in recovery of hydrochloric acid from pvc wastes. The process begins with carbonization of plastic wastes for about 40 minutes at 280°C to 300°C to remove the chlorine from vinyl chloride. Hydrochloric acid generated by the process is absorbed by water.

CO_2 and H_2S may be removed using aqueous ammonia with production of ammonium sulfate which may be recovered for sale as a fertilizer. Monoethanolamine is used to remove CO_2 from flue gas for its recovery or for the purification of flue gas to nitrogen.

SO_2 can be removed by liquid absorption and purified for later collection, compression, and resale. The Sulphidine process uses a mixture of tylidine and water and produces by-products of sodium sulfate and pure SO_2. In another process designed to remove SO_2 from smelter gas, dimethylaniline is the absorbent used to remove the gas from the stream, producing a by-product of either dilute sulfuric acid or liquid SO_2 (Ross, 1972).

Within the past several years, a great deal of work has been done with gas/solid absorption systems, particularly with regard to sulfur dioxide (SO_2) removal. These processes should not be considered for streams of low flow, however, the catalytic oxidation process developed by Monsanto passes flue gas, following particulate removal, through a vanadium pentoxide catalyst. This results in the production of a 77 percent sulfuric acid solution.

In the alkalized alumina process developed by the U.S. Bureau of Mines, flue gas is passed through a fluidized bed of alkalized alumina. The bed reacts with the SO_2 in flue gas at temperatures of 300 to 350°C, resulting in its conversion to sulfate. After treatment with a suitable reducing gas, hydrogen sulfied (H_2S) gas is produced. The H_2S is processed through a Claus plant to bring about its conversion to elemental sulfur (Ross, 1972).

5.3 ADSORPTION

Adsorption on carbon has been known for a long time (Hasler, 1974), however, its application in the field of municipal and industrial wastewater treatment has become common only in recent years.

The term activated carbon applies to any amorphous form of carbon that has been specially treated to give high adsorption capacities. Basically there are two forms of activated carbon: powdered and granular. The former are particles that are less than U.S. Sieve Series No. 50, while the latter are larger (U.S. EPA, 1971a). Typical raw materials, from which activated carbon is made include coal, wood, coconut shells, pulp mill residues, petroleum base residues, and char from sewage sludge pyrolysis. These carbon materials are activated through a series of processes which include (Cheremisinoff and Morressi), 1978:

1. Removal of all water (dehydration);
2. Conversion of the organic matter to elemental carbon driving off the non-carbon portion (carbonization; and
3. Burning off tars, methanol, and other by-products at high temperatures (750-950°C) (activation).

Adsorption involves the interphase accumulation or concentration of substances at a surface or interface (Weber, 1972). The process can occur as an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being adsorbed is called the adsorbate while the adsorbing phase is termed the adsorbent.

There are two types of adsorption: physisorption and chemisorption. The former occurs because of weak Van der Wall's forces while chemisorption is a result of a chemical interaction between the adsorbent and the adsorbate. Physisorption is characterized by a relatively low energy of adsorption and may be multilayered. Chemisorption processes, however, exhibit high energies of adsorption.

The adsorption process can be affected by many factors, some of these include (Cheremisinoff and Morressi, 1978):

1. The physical and chemical characteristics of the adsorbent, i.e., surface area, pore size, chemical composition, etc.
2. The physical and chemical characteristics of the adsorbate, i.e., molecular size, molecular polarity, chemical composition, etc.
3. The concentration of the adsorbate in the liquid phase.
4. The characteristics of the liquid phase, i.e., pH, temperature, etc; and
5. Residence time of the system

5.3.1 Factors Affecting Adsorption: Inorganics

The surface area of the activated carbon plays a critical role in the removal of inorganics by adsorption. It may typically range from 500 to 1400 m^2/g with some carbons having surface areas up to s,500 m^2/g. Another important parameter affecting the adsorption process is the chemical nature of the surface of carbon. This chemical nature varies with the carbon type and can influence attractive forces between molecules. For the most part, activated carbon surfaces are nonpolar making the adsorption of inorganics difficult (Cheremisinoff and Morressi, 1978).

5.3.2 Regeneration Operation: Inorganics

Wastewater treatment with activated carbon involves two major separate process operations, namely, contacting and regeneration. During the first operation, the water is contacted with the carbon. Impurities are removed from the water by adsorption to carbon. After a given period of time, the adsorptive capacity of the carbon is exhausted. Then the carbon is taken out of service and regenerated, usually, by combustion. During this process, the impurities are adsorbed for potential recovery.

On some systems an additional process operation namely, backwashing may be necessary. It is required in cases where suspended solids are trapped in carbon beds causing severe head losses. Backwashings are more frequent for downflow contactors, which may be designed for suspended solids removal also.

Regeneration of spent carbon is practiced in cases where a large quantity of carbon is used. Thermal reactivation is the most common method used for regeneration of carbon. Other methods include alkaline regeneration for acid adsorbates, acid regneration for basic adsorbates, stream regeneration and solvent regeneration.

5.3.3 Recycle, Recovery and Reuse Applications: Inorganics

Activated carbon is used in water treatment to remove organics that cause odors, tastes and other detrimental effects. It is used in municipal and industrial wastewater treatment for removal of dissolved and/or hazardous organics. In addition, activated carbon is used as a recycling media for the recovery of valuable substances from certain industrial effluents.

The major applications of activated carbon in wastewater treatment include:

1. Silver and Gold Processing Plants (Cheremisinoff and Morrissi, 1978).
2. Inorganic Chemical Industry (Suisi, et al. 1970; Taushkano, et al. 1974).
3. Electroplating Industry (U.S. EPA, 1971b; Smithson, 1971).
4. Refineries (Loop, 1975)
5. Various Industries With Metal-laden Effluents (Linstedt, et al. 1971; Cheremisinoff and Habib, 1972; Netzer, et al. 1974).

Various inorganic substances from the above-listed industries are removed from the effluents and possibly recovered through the use of activated carbon treatment. The degree of adsorption of these inorganics on carbon and the final recovery may vary from species to species. The major group of inorganics which are recovered through activated carbon treatment are metals. By product recovery is advantageous for valuable substances and also in cases where regeneration of carbon results in low recovered adsorptive capacity of carbon.

5.3.4 Factor Affecting Adsorption: Organics

The adsorption capacity for organic solutes is thought to be a function of:

1. Adsorbate properties such as functionality, branching or geometry, polarity, hydrophilicity, dipole moment, molecular weight and size, and aqueous solubility.
2. Solution conditions, including pH, temperature, pressure, adsorbate concentration, ionic strength, and the presence of background and competitive solutes.

3. The nature of the adsorbent, such as surface area, pore size and distribution, surface distribution, and surface characteristics (Miller, 1980a).

5.3.5 Adsorbents-Activated Carbon and Resins: Organics

Activated carbon is a term used to describe materials prepared from raw materials such as wood, lignite, coal, bone petroleum residues, and nut shells which exhibit a high degree of porosity and extremely large internal surface area. Activated carbon has found a wide commercial application as an adsorbent due to its ease of production, reasonable cost, and regeneration capability.

Little quantitative information is known about the surface characteristics of carbon and its influence on organic adsorption selectivity. These characteristics are important to adsorption of specific solutes. Two types of surface interactions are thought to predominate. The first is that of van der Waal force interactions, hydrophobic in nature, and occurring on a majority of the surface. The second type occurs at the more reactive edges, and may be characterized by positive physical and perhaps chemical interactions due to hydrogen bonding and electrostatic forces. This second type of interaction occurs at a small fraction of the total surface area. Specific adsorptions will result from the presence of oxides, hydroxyls, and other groups on the surface. Activated carbons produced by different processes probably differ in their adsorptivity as a result of their different energy potential and the extent of their heterogeneous sites (Miller, 1980a).

Snoeyink, et al. (1979) found that the nature of sorption sites can vary significantly between different carbons, even though they have similar total surface areas. Their results indicate that phenol sorbs more extensively on a coal-based carbon than on a coconut-shell carbon at low concentrations. Recommendations were made for study in the areas of the sorptive behavior and characteristics of activated carbon, the types of functional groups on the surface, and possible alteration of the surface to produce a more efficient adsorber for a given purpose.

El-Dib, et al. (1979) states that little is known about the adsorption characteristics of soluble aromatic hydrocarbons on granular carbon and its efficiency in the removal of such organics. In a study of benzene, toluene, o-xylene and ethylbenzene, they found that these compounds were adsorbed in accordance with the Freundlich model, and that the parameters K and 1/n reflect the effects of chemical structure, solubility, and competitive interactions on the adsorption process. In the case of a mixed-solute solution, they found that uptake of each compound was considerably reduced, although the order of adsorption was the same.

The use of polymeric adsorbent resins should be considered in cases where the economics of solvent or chemical regeneration of the adsorbent is favorable. Polymeric adsorbent resins are similar in size, shape, and appearance to conventional ion exchange resins, but differ in the respect that they contain no ionically functional sites. There are two basic families of adsorbent polymers available: one is based on crosslinked polymethacrylate structure, while the other is based on a crosslinked polystyrene structure (Fox, 1979). Although capital costs of synthetic adsorbent systems and those of activated carbon are comparable, operating costs indicate that polymeric adsorbent methods are more economical than carbon systems when the level of dissolved organics is high (Stevins and Kerner, 1975). An attractive feature of synthetic resins is that they can, at least theoretically, be designed and manufactured for a specific adsorption application (Kim, et al. 1976).

It has been demonstrated that Amberlite XAD polymeric adsorbents can remove substantial quantities of phenolic compounds from aqueous solutions with the added benefit of being easily regenerable with nonaqueous solvents or caustic solution. This permits the recovery of a useable form of phenolic material in many cases. Crook, et al. (1975) studied the results of flow rate, concentration, temperature, and pH on phenol removal. They found that at 6700 ppm influent phenol concentration, the capacity of Amberlite XAD-4 polymeric sorbent for phenol is (to 1 ppm leakage) 87 g/l, while at 3000 ppm influent concentration the capacity decreases to 72 g/l. Cumulative phenol leakage was found to be slightly higher at 5°C than at 25°C. Although flow rates were varied from rates of 2 to 4 bed volumes per hour, the resultant phenol leakage was 0.1 ppm or less up to the break point. pH values of 3 and 6.45 were used to determine the effect of pH on phenol removal. Results indicated that slightly better performance may be obtained in the lower pH range. In another experiment Crook, et al. (1975) tested the effect of bed depth on removal of p-nitrophenol and found that a 15 inch bed depth column of XAD-7 resin does not afford substantial improvement over a 9 inch bed depth in either leakage or capacity at the flow rate of effluent studied. Removal of Bisphenol A was also studied using both the XAD-4 and XAD-7 resins. These resins differ in polarity. It was found that the XAD-4 resins successfully treated 33.5 bed volumes while the XAD-7 treated 16 volumes. These experiments were mentioned to illustrate the many variables which may or may not effect removal of an organic compound from an aqueous solution.

The use of carbon adsorption, and more recently, polymeric resin adsorption for removal of organic contaminants from wastewater has proven to be effective. However, DiGiano (1980) states, with reference to carbon adsorption, that there are many unanswered questions regarding control of process performance and that part of the problem originates from the variability in composition and concentration of contaminants in waste streams. Regarding polymeric resins, complex reactions involved in the adsorption process can only be partially predicted. Laboratory feasibility studies, and in some cases pilot studies under actual use conditions, are generally needed before the appropriate resin and operating conditions for a specific application are defined (Fox, 1978).

5.3.6 Regeneration and By-Product Recovery: Organics

Himmelstein, et al. (1973) reviewed the various methods of in-place regeneration of activated carbon. Reactive regeneration, by which phenol is desorbed from the column by reaction with caustic soda, has been practiced. In the plant where this took place, the regenerant solution was suitable for recycle without further treatment and an excellent example of an opportunity for recovery. Phenol is recovered in the product stream, and the residual caustic is used as a component in phenol production.

Solvent regeneration involves the use of a solvent phase to desorb the organics from the carbon, and is removed as in conventional recovery systems by steam. The solvent may be recovered for reuse in subsequent regeneration while the desorbed materials may be reintroduced into the process or refined for reuse or sale. In some cases, the regenerated steam may be recycled without further processing. Unlike reactive regeneration, solvent regeneration is feasible in cases where direct recycle of a regenerant stream is not feasible. Separation of the solvent and recovered material may be accomplished by distillation, extraction, decantation, or precipitation. Recovery by steam treatment has been demonstrated by laboratory studies to be feasible for waste streams such as those containing acetic acid, aromatic acids, chlorinated aromatics, phenols, alcohols and esters.

Due to the high binding energies of carbon, thermal reactivation of activated carbons is often the only successful means of regenerating the carbon. Thermal regeneration also leads to destruction of the adsorbed species, making their recovery impossible. Baker, et al. (1973), however, describes the use of carbon adsorption of sulfite effluent prior to oxidation, followed by chemical regeneration of cresylics and return a valuable product to the process in a full-scale plant situation.

Jensen (1980) describes a semi-continuous activated carbon system for removal of dissolved acrylic monomers from wastewater. By using such a unit, acrylic monomers can be recovered at some value, and the wastewater is upgraded for reuse. Three carbons were compared for suitability for removal of COD loading in these wastewaters.

Phenolic compounds are bound to adsorption polymers by van der Waal's forces. Parmele has shown this by measuring the enthalpy of binding mono and dichlorophenols to Amberlite XAD-4 at -4 to -6 kcal/mole. This is within the range for physical forces holding the phenolic to the adsorbent. Small energy inputs are required for desorption, the phenols can be easily recovered by regenerating the resin. This is the key to the value of resins for waste material recovery. Fox and Himmelstein (1974) discuss several applications of polymer adsorption and regeneration for the recovery and recycle of phenol, para-nitrophenol and phenoxy acid pesticide.

Stevens and Kerner (1975) state that the binding energies of synthetic resins are lower than those of activated carbon for the same organic molecules.

This would make recovery of organics from resins more attractive than from carbon, due to smaller energy inputs needed for desorption. Fox (1979) lists organic solvents including acetone, methanol, isopropanol, and inorganic solvent systems such as steam, aqueous caustic solutions, and aqueous acids for resin regeneration.

Chlorinated pesticides such as endrin, DDT, 4-D, 2, toxaphene, and polychlorinated biphenyls can be efficiently removed by adsorption onto an adsorbent resin with polystyrene structure. One plant which manufactures 2, 4-D, and related herbicides practices recovery of phenoxy herbidicides and their intermediates for recycle to the process. Regeneration is performed with saturated steam. The resin is regenerated with methanol, and the herbicide and its intermediate is recovered by distillation.

Aqueous effluents from vinyl chloride and other chlorinated hydrocarbon manufacturing plants contain up to 1% of a mixture of ethylene dichloride, chloroform, and/or carbon tetrachloride. After steam regeneration of the resin, the collected condensed organic phase can be either reused in the plant or incinerated. Effluent streams from the production of benzene, toluene, and xylene are usually contaminated by these organics. Recovery of these compounds is carried out in a process scheme similar to that for chlorinated hydrocarbons. From these examples, it is evident that polymeric adsorbents may be used by industry for removal and recovery of chlorinated pesticides, phenols, aliphatic chlorinated hydrocarbons, benzene, toluene, and xylene (Fox, 1979).

5.3.7 Predicting Adsorption: Organics

Several approaches have recently been developed to relate characteristics of molecular structure or a chemical property such as solubility to adsorption potential for activated carbon. Manes and Hofer applied the Polanyi adsorption potential theory, originally developed to describe gas-solid adsorption. Follow up studies have shown this technique to be successful for describing single, bi- and tri-solute equilibria, but testing is still limited. Problems with the application of the theory include the fact that the solubilities of many organic compounds of interest are not readily available, while other compounds are relatively soluble, requiring that a more complicated model be used (DiGiano, 1980).

Although few multicomponent studies have been done, equilibrium models have been developed. These include the Langmuir Competitive Model, which maintains that adsorption sites are available to all adsorbates; the Langmuir Semi-Competitive Model, which states that some sites are available to all absorbates while others are just available to most adsorbable material; and the Ideal Solution Theory, which is developed from thermodynamic consideration.

Each model was tested on its own bisolute systems, and little has been done to compare the models on additonal systems. In a column study, all three were unsuccessful in predicting relative loadings.

A predictive technique developed by Keinath, et al. to predict individual component behavior was based on the assumption that increasing Langmuir b constants are related to stronger adsorption. Tests were limited, and more work is necessary. This method could possibly predict the preferentially adsorbed compound.

It may be possible to simplify the description of competitive systems by grouping adsorbable components into a few broad classes according to their equilibrium adsorption behavior. A single, synthesized equilibrium isotherm for each class would be used in simulation of competitive adsorption. For this to occur, a method must be found to account for competitive behavior which does not conform to that expected based upon single component isotherm. Crittenden and Weber found this to occur in a phenol-dodecylbenzenesulfonate (DBS). Phenol was absorbed to a far greater extent in a single solute system, but competition favored adsorption of DBS (Arbuckle and Romagnoli 1980).

Arbuckle and Romagnoli (1980) used isotherm constants and chemical solubilities to predict the preferentially adsorbed compound in 22 bisolute activated carbon systems. Solubility predicted the preferred compound for 20 systems, while the Freundlich K constant was correct for all systems. The amount of nonpreferred material displaced was in correlation with the absolute difference in K; the greater the difference, the more material displaced. This information is useful in predicting whether or not a chemical will be concentrated in a column's effluent and to minimize carbon consumption by knowing the order the compounds leave the column (important when removal of a specific component is desired). They recommend additional studies to (1) determine effects of different relative solute concentrations, (2) evaluate a wider variety of chemicals, and (3) evaluate multi-solute systems.

Because many of the equilibrium theories and theories for predicting competitive adsorption currently in use are based on gas and vapor phase adsorption, they have one major limitation: the presence of solvent during solute adsorption is ignored. Belfort and Altshuler have adapted the solvophobic theory, a general thermodynamic treatment for describing the effect of various solvents on reaction rate constants and equilibria, to adsorption (Miller, 1980b).

By using the same type of adsorbent and identical solution conditions, different workers have attempted correlation of single-solute adsorptive capacity with molecular weight, solubility, functionality, and position of substitution. Although several general trends are indicated, no one parameter has emerged in predicting the dominant effect of adsorption. It is probably not reasonable to expect a one-dimensional approach to provide a consistent predictive correlation (Miller, 1980b).

Given single-solute or multisolute adsorption equilibrium, a reasonably good description of multicomponent behavior may be obtained. There is a need for an equilibrium adsorption theory which can predict, without experimental observations, the preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions (Miller, 1980a).

5.3.8 Recycle, Recovery, and Reuse Applications

Compounds Recovered:

Polysterene Adsorbent Resins
Polychlorinated Biphenyls
Ethylene Dichloride
Chloroform
Carbon Tetrachloride
Benzene, Toluene, Xylene
Phenols
Para-Nitrophenol
Phenoxy Acide Pesticides
Chlorinated Pesticides
Aliphatic Chlorinated Hydrocarbons
Activated Carbon
Benzene

Toluene
Xylene
Ethylbenzene
Acrylic Monomers
Phenol
Acetic Acid
Aromatic Acids
Chlorinated Aromatics
Alcohols
Esters
Cresylics
Hydrocarbons
Tar Acids
Tar Bases

Industries in which Recovery by Adsorption has been applied:

Pesticide Manufacturing
Organic Chemical Manufacturing

Petrochemical Industry
Paint Industry
Coke Plant

5.4 ADSORPTION: GASES

The potential areas for future research in the adsorption of gases are:

1. Adsorbent Properties
2. Regeneration Methods
3. Modeling Theory

A brief description of these areas follows:

1. Adsorbents

In the recovery of organic gaseous air pollutants, activated carbon has been by far the most effective adsorbent used. However, the adsorptive capacity of any adsorbent is limited by:

- the surface area available for adsorption
- pore size and distribution
- temperature and pressure of operating conditions
- concentrations of influent organics
- desired recovery level (collection efficiency)

Exploration of the effect of different catalysts on the adsorbing surface could result in a more effective and easy way to desorb (these catalysts should inhibit stronger affinity onto the adsorbing surface for material to be recovered).

Impregnation of adsorbents has proven successful in some cases and could be further studied.

2. Regeneration Operation

In the regeneration process, modification of the systems and operating procedures used in solvent recovery have already resulted in an improved collection. However, this recovery is rarely optimized under given operation conditions.

Vacuum stripping (Kenson, 1979) with steam has been recently been shown to be a successful method of recovering hydrocarbons. However, some problems arose due to corrosion effect of the adsorber vessel, e.g., many of the materials recovered hydrolyze slightly to generate HCl when exposed to chlorinated solvent. A better understanding not only of physical properties but also of chemical properties of both adsorbent and adsorbate is necessary.

The improved design of existing systems and their regeneration control (this control should be based on regeneration capacity rather than time cycle) would certainly give a better regeneration rate. It can also result in corrosion reduction (Parmele, et al. 1979).

An investigation of the regenerating media will shed more light on the right choice of the regenerating agent.

Methods of predicting binding energy of solvent molecules to the adsorbing surface (the problem arises here when dealing with competing molecules from a mixture of solvents) (U.S. EPA, April 1978) are needed.

3. Theory and Modeling

Theoretically, optimum adsorption is accomplished under the following conditions:

- low base-line concentration of effluents
- containment of breakthrough emissions
- efficient recovery of desorbed organics
- containment of organics exhausted during cooling and drying cycle

Since adsorption capacity is affected both by the properties of the adsorbent and those of the adsorbate, and the conditions under which they are contacted, a better understanding of the properties of both adsorbent and adsorbate would be beneficial.

A better method for predicting the preferential adsorption of competing molecules (in a solvent mixture) and how they could be desorbed more effectively is needed.

5.4.1 Adsorbents and Their Properties

Each adsorbent has a preferential adsorption for adsorbates based on its adsorptive capacity and affinity for different materials (adsorbates). It is this characteristic (selectivity) that is important for each adsorbent. Selectivity and capacity can change the suitability of an adsorbent for air pollution control usage, limiting some for special conditions, while allowing broader application of others.

Chemical composition, ratio of surface area to volume, pore size and distribution and granule (particle) size are the most important characteristics of an adsorbent. The adsorption capacity is a function of these characteristics, and is better defined with adsorption isotherms and/or adsorptive capacity data at different operating conditions.

Depending on their chemical constitution and pore size distribution, adsorbents can be classified into the four categories which are discussed below.

1. Chemically Reactive Adsorbents

   These adsorbents can also be impregnated with chemically reactive compounds. The adsorption operation by these adsorbents is highly selective and tends to be irreversible. It is an exothermic reaction which stops when all active sites on the surface have reacted. The surface is then covered with a unimolecular layer of vapor.

Example: Soda lime (with or without activated carbon) is used in the chemisorption of ethanoic acid, acetonitrile, acrylonitrile, alkyl chloride, and vinyl propyl desulfide.

2. Polar Adsorbents

The adsorption process is caused by Van der Waal's forces on a chemically non-reactive surface, having polar properties. These adsorbents are less selective and the process is reversible. The heat released is about 10 kcal/g. mole.

The adsorbing surface is saturated by several molecule layers. At fixed vapor pressure, the adsorption decreases with increasing temperature.

Examples: Silica gel and activated alumina both have strong selectivity for polar compound (H_2O, olefins) and are generally used in separation and purification processes.

The dielectric constant and the dipole moment of molecules characterize their adsorption affinity. Affinity decreases with decreasing dielectric constant and decreasing dipole moment. However, it also decreases with increasing Van der Waal's force.

The application of these adsorbents is mainly limited to the drying of gases due to their strong affinity for water. Desorption generally occurs with regenerative water steam followed by drying of adsorbent at higher temperature.

3. Non Polar Adsorbents

The most important adsorbing non polar solid is carbon, which is effective in attracting non polar molecules such as hydrocarbons. Activated carbon is used to remove hydrocarbons, odors and similar trace contaminates from gas streams. Activated carbon must be specially treated before use, because adsorption of water vapor is very sensitive to the presence of polar impurities. Activated carbon usually contains S_1O_2, Al_2, Fe_2O_3, NaOH, KOH and adsorbed oxygen.

4. Molecular Sieves

Molecular sieves are available as having polar and non polar properties. They are effective in adsorbing low molecular weight or unsaturated hydrocarbons from dry air at low concentrations. Adsorption of low molecular weight saturated hydrocarbons (methane, ethane) by activated carbon is more effective than by molecular sieves, but too poor in any case for effective pollution control.

5.4.2 Regeneration Operation: Gases

The adsorbent bed must be regenerated for reuse after breakthrough has been reached. The recovery of organic compounds generally occurs by stripping (Kensen, 1979) them into easily condensable streams of gas. The conventional methods of regeneration involve heated air, heated inert gas or heated steam, depending both on the adsorbent and the adsorbate properties. In the case of use of noncondensable gas as a regenerative agent, the desorbed material can be disposed of in several ways (U.S. EPA, April 1973). When using steam as a regenerating agent many pollutants cannot be economically recovered due to their high steam to solvent ratios. Adsorption/steam regeneration with solvent recovery has been conventionally used in concentration above 500 ppm. Using distillation on partially or totally soluble compounds is costly, and moreover disposal of this polluted steam condensate can constitute another form of environmental pollution if disposed of into sewers.

Some commercially available systems use hot nitrogen or some other melt gases to desorb the organics from the carbon. Vaporized organics condense to a liquid, and are reused in the process or as a supplemental fuel. The inert gas is then vented or reheated and recirculated to the adsorber.

Regeneration can also be accomplished by vacuum stripping (Kenson, 1979). In a vacuum system, pressure is reduced to a point below the original partial pressure of adsorbed material. Regeneration takes place rapidly at extremely high concentrations. This method is used when there is hydrolysis of the organics or formation of azeotrope with water, if the organics do not respond sufficiently to low pressure steam regeneration, or if they have concentration above combustion range. Inert gas regeneration is also used under the above conditions. A cooling and drying period is necessary before the bed can be reused for recovery.

Recent efforts of process engineers and equipment designers have been mainly oriented toward improving the economics of solvent recovery operations. So far the principal areas of interest have been (U.S. EPA, April 1973):

- Decrease in energy or fuel requirement for regeneration
- Reduction of pressure drop during adsorption phase
- Increase of adsorptive capacity by utilizing residual capacity of adsorption zone
- Improved methods for ecovery of desorbed solvents.

5.4.3 The Adsorption Cycle: Gases

The adsorption cycle is a function of the adsorbent life, the bed length, and the mass transfer zone. Vapor-phase activated carbon adsorption has gained favor as a method of recovering valuable solvents from industrial emission sources. The adsorption is usually a batch operation with multiple beds. Upflow design is generally avoided because carbon particles can become entrained in the exhaust at higher superficial velocities. The gas stream is pretreated to remove solids (dust, lint), liquids (droplets or aerosols), or vapor (high inlet concentration or high boiling components) since these can hamper performance. Pretreatment with condensers is generally advantageous in reducing inlet concentrations. The following objectives are required for high removal efficiency (Parmele, et al. 1979).

- Low base-line effluent concentrations (usually less than 10 ppm).
- Containment of breakthrough emissions. This is done by avoiding premature breakthrough or by sending material emitted during breakthrough to another vessel hooked up in series.
- Efficient recovery of desorbed organics. This is usually achieved by condensing the vapors and recycling the noncondensables from the condenser back to the inlet of the online adsorber.
- Containment of organics exhausted during the cooling and drying cycle. This cycle prepares the carbon bed for renewed service.

5.4.4 Adsorption Theory and Modeling: Gases

The adsorption operation is a method of controlling gaseous impurities from industrial gas streams. The gas molecule is retained on a solid surface by physical or chemical forces. These two types of adsorption are described as follows:

Physical Adsorption

Physical adsorption occurs when gas molecules attract and hold each other forming a multilayer of gas molecules (not more than a few molecules thick) on the solid surface area. This is caused by Van der Waal's forces at the gas-solid interface. The process is exothermic (10 kcal/g-mole) in which the free energy of the gas decreases.

Chemical Adsorption--Chemisorption

This is also an exothermic process (10 kcal/g-mole) in which gas molecules are held to the adsorbing surface by chemical bonding (sharing of electrons). Chemisorption results in only one layer of molecules on the adsorbing area available.

The adsorption phenomenon occurs in two stages. First, there is rapid and 100% removal efficiency, then breakthrough happens when this removal efficiency falls below 100%. At this point outlet concentration is equal to the inlet concentration.

A single vapor consists basically of a solvent and air. However, when water vapor is present in the vapor, the mixture becomes ternary. At high concentrations of water vapor in the mixture, interference occurs among the solvent molecules and the water molecules adsorbing to the activated sites. This same phenomenon occurs, although in a different way, in a mixture of two or more solvents.

The presence or absence of water may be the deciding factor in choosing the adsorbents. For example, when water vapor is present in a gas stream, adsorption of organic vapors cannot be effectively achieved with polar adsorbents (U.S. EPA, April 1973). The effect of the competition of solvents on adsorption efficiency are not well understood.

In order to arrive at an optimum interaction between adsorption and regeneration, it is necessary to understand the factors that affect the performance of the adsorbent (activated carbon) during these two operations. So far there is no method that satisfactorily predicts the performance of adsorption systems from theory, although several have been proposed.

It has been found that the average residence time of a molecule on the surface increases with decreasing temperature and/or decreasing partial pressure of the vapor.

Freundlich described the adsorption phenomenon in its early stage by the following equation (U.S. EPA, April 1973):

$$V = k\ P^{1/n} \tag{5.1}$$

where: k and n are Freundlich constants

This equation applies also to chemisorption. This is common when an impregnated carbon is used. The most common theory that is valid in describing adsorption in the smallest pores is Polyanyi's potential (Parmele, 1979) theory which holds that for a fixed amount of adsorbed material, the free energy of adsorption, ΔF, is a constant and is a function of the relative vapor pressure (P/P_o).

$$\Delta F = \underline{R^{T}}\ \ln\ ({}^{Po}/P) \tag{5.2}$$

where: T = absolute temperature
Po = vapor pressure
P = partial pressure
R = ideal gas law constant

This relationship makes the use of isotherms possible in predicting relative vapor pressures of a material in equilibrium with carbon at a variety of temperatures.

5.4.5 Application of Adsorption Operation in Industries: Gases

Adsorption is a particularly recommended and useful technique when:

1. The solvent (containment) has recovery value.
2. The solvent is in extremely low concentrations.
3. The solvent gas may be noncombustible or nonflammable (below 25% of its lower explosive limit)

Some of the applications of adsorption are used in:

- surface coating (fabric or filter)
- film casting
- metal degreasing
- dry cleaning
- printing
- rendering
- food processing
- chemical processing
- paint spray booth
- bake ovens

Some of the principal adsorbents used are:

- activated carbon: hydrocarbons, odors
- silica gel: dehydration of gases
- activated alumina (aluminum oxides): dehydration
- molecular sieve (synthetic zeolites): SO_2, No_x, Hg

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CHAPTER 6

SECTION II

MOLECULAR SEPARATION

6.1 INTRODUCTION

The following chapter examines the "Recycle, Recovery, and Reuse Applications" of several molecular separations processes. The processes included in this chapter are:

1. Reverse Osmosis
2. Ion Exchange
3. Ultrafiltration

Ultrafiltration and Reverse Osmosis are commonly referred to as membrane processes. A membrane is defined as a phase which acts as a barrier to flow of molecular or ionic species between other phases that it separates. On the other hand, Ion Exchange can be considered a sorption process (Sundstrom and Klei, 1979). In Ion Exchange, there is a reversible interchange of ions between a liquid and solid (the transfer of ions between phases occurs at the solid surface) where there are no permanent changes in the structure of the solid.

Chapter 6 is divided into two major sections. The first section of the chapter will examine the recycle, recovery, and reuse applications for organic compounds as related to the two membrane processes listed above. The second section of the chapter will then examine the recycle, recovery, and reuse applications for inorganic compounds as related to the ion exchange and reverse osmosis processes.

6.2 ORGANIC COMPOUNDS

6.2.1 Membrane Processes

Membrane ultrafiltration and reverse osmosis are hydraulic pressure activated processes capable of separating solution components largely on the basis of molecular size and shape, and involve neither a phase change nor interphase mass transfer. By proper membrane selection, it is possible to concentrate, purify, and fractionate many components of a solution. These processes are particularly attractive due to the fact that the sole energy requirement is the compression energy of the feed liquid.

Reverse osmosis generally applies to the separation of low-molecular weight solutes such as salts, sugars, and simple acids from their solvent. The driving pressure for efficient separation must exceed the osmotic pressure of the solute in solution. This may require pressures of 500 to 2,000 psi. Ultrafiltration is the term used for separation of higher molecular weight solutes such as proteins, starch, natural gums, and other complex organic compounds, as well as colloidally dispersed substances such as clays, pigments, minerals, latex particles, and microorganisms, from their solvents. Osmotic pressure of the solute in these systems is usually negligible, and typical operating pressures range between 5 and 100 psi. Although the processes are related, ultrafiltration does not require the high operating pressures which are needed to overcome the high osmotic pressure differential across a reverse osmosis membrane (Porter, 1972). Both systems, however, are worth consideration in treating many streams to produce a concentrate suitable for reuse.

6.2.1.1 Membrane Characteristics

The membranes for both ultrafiltration (U.F.) and reverse osmosis (R.O.) can be made from various synthetic or natural polymeric materials, ranging from hydrophilic polymers such as cellulose, to hydrophobic materials such as fluorinated polymers. Polyarylsulfonates and inorganic materials have also been introduced to deal with high temperatures and pH needs (Berkonitz, et al. 1976).

The use of cellulose acetate membranes or their derivatives imposes some limitations. Operating temperatures must be restricted to less than 110°F to avoid hydrolysis of the cellulose acetate. Cellulose acetate membranes normally are limited to operating within the pH range of 3 to 8. Strongly acid or alkaline solutions will cause rapid membrane degradation (Ruver, 1973). Certain noncellulosic membranes have temperature capability of 230^{o}F and pH capability between 1 and 12 (Porter, 1972).

Membranes having an anisotropic structure, with poses roughly conical in shape are not subject to internal fouling problems. The smallest pore diameter remains at the membrane surface. A solute which finds its way into the membrane is likely to pass through to the other side of the membrane, since pore diameter increases from entrance to exit (Porter, 1973).

Ohya, et al. (1979) studied the effect of evaporation period at casting stage on the water flux and membrane structure of a cellulose acetate butyrate membrane. With short evaporation time, membranes with large fingerlike cavities were formed. No holes were formed on the upper surface. Water flux properties were low. Upon long evaporation periods, a solid structure was formed. These membranes tended to have high flux properties. No explanation was offered for the relationship between membrane structure and its characteristics.

6.2.1.2 Membrane Rejection and Flux

According to Spatz (1973), the rejection of organics is based on a sieve mechanism related to the size and shape of the organic molecule. In the case of organics which act like salts, a combination of rejection mechanisms may occur, since salts are rejected because of the physiochemical reaction with the membrane surface.

Sourirajan and his coworkers have studied organic separation by cellulose acetate membranes, and found solute separation to be dependent on its ability to form hydrogen bonding with the membrane materials (Chian and Fang, 1977).

Chian and Fang attempted to establish generalized criteria conducted with five membrane types and dozens of organic compounds, and found that the physio-chemical criteria and pressure effects on solute separation established with the cellulose acetate membrane are generally valid with other commercially feasible membranes. For instance, for membranes having appropriate surface structure, pore size, etc., the more nonpolar the membrane, the better the solute separation will be, particularly for low molecular weight polar organic solutes. The choice of nonpolar membrane materials, however, may produce a decrease in water flux (Chian and Fang, 1977).

Once a membrane is selected which provides the desired removal of solute, the remaining important operating parameter is membrane permeability or flux. Initially, membrane resistance controls flux. However, when the solute begins to build up along the membrane surface, a polarized layer, or gel forms. When the gel concentration exceeds a critical level, gel resistance controls mass transfer (Nelson, 1973).

In the presence of large surfactant concentrations, almost instantaneous fouling can take place, a condition to which only low surface energy polymers are immune. Fouling can be controlled to a high degree by high circulation velocities, proper membrane configuration, and control of process fluid composition (Mir, et al. 1977).

Fenton-May and his coworkers (Fenton-May, et al. 1972) found that at low flow rates, the primary resistance to membrane transport is offered by a hydrodynamic boundary layer produced by polarization, and that mass transfer is controlled by membrane resistance and gel precipitate at higher flow rates.

For both reverse osmosis and ultrafiltration, Fenton-May osmosis and his coworkers found an increase in permeate flux of 40% for every 20°F increase in feed temperature.

In studying pressure effects, they found a completely linear relationship between applied hydrostatic pressure and membrane pure water flux up to a pressure of about 450 psi, indicating that, within this range, resistance of the membrane itself to mass transport is pressure independent. When a whey or skim milk feed was used, however, an increase in operating pressure increased solute rejection, a result of an increase in resistance to solute transport of the protein gel layer.

Since membrane flux rates are for the most part limited by concentration polarization or gel resistance, various techniques have been applied to reduce this problem, generally by cross-flow fluid management techniques. It has been reported that by operating above a critical cross-flow velocity, gel resistance is minimized and flux increases with increasing pressure. An economic optimum must be reached between power costs necessary to maintain the desired cross-flow velocity and shear effects and membrane area costs determined by membrane flux.

6.2.1.3 Prediction of Binary-Solute Behavior

Fels (1972) studied the permeation and separation of binary organic mixtures using polyethylene membranes, and found that ideal behavior was not exhibited. The deviation from ideal behavior increased as the difference in interaction behavior between the liquids and the polymer (as measured by a solubility parameter difference) increased. The purpose of this study was to contribute to the ideal of predicting separation behavior of membranes from a knowledge of the individual component behavior of the system. 6.2.1.4

6.2.1.4 Statement of Limiting Technology

1. Membrane Characteristics
    - The relationship between membrane structures and their rejection and flux properties are not fully understood.
    - A need exists for better membranes which will have longer life under the varying operating conditions of temperature, pressure, pH, and flow rate and which are less prone to fouling and chemical degradation, have higher water flux rates, and good solute rejection characteristics.
2. Membrane Rejection and Flux
    - The membrane properties of flux and rejection rarely control process performance. Performance is usually limited by concentration polarization or gel formation at the membrane surface, and is less efficient than membrane controlled performance. The answer to the problem may be found in the study of one of three areas: improved hydrodynamics result-

ing in higher shear forces; the interaction of gel layers, or dynamic membranes; with the membrane, or the interaction between the membrane polymer and feed.

- Little is known about the possibility of reducing the influence of undesirable dynamic membranes formed from feed constituents. It may be possible to purposely add species capable of forming gel layers, or secondary membranes, which may enhance membrane processes, to the feed.

6.2.1.5 Resource, Recovery, and Reuse Applications

- Production of protein concentrates and isolates from soy whey.
- Concentration and fractionation of cheese whey and skim milk.
- Oil-emulsion concentration.
- Polyvinyl alcohol recovery and concentration.
- Recovery of protein and pectin from sugar beet wastes.
- Recovery of lignin and ligno-sulfonates from pulp and paper extraction effluent.
- Recovery of polyglycols from polyurethane production processes.
- Recovery of chocolate wastes.

6.3 INORGANIC COMPOUNDS

This section of Chapter 6 examines the recycle, recovery, and reuse applications for organic compounds as related to the ion exchange and reverse osmosis processes. 6.3.1

6.3.1 Ion Exchange

Ion exchange is a process in which ions held by electrostatic forces to charged functional groups on the surface of a solid are exchanged for ions of similar charge in a solution in which the solid is immersed (Weber, 1972). Basically in this process, the ion exchanger is contacted with the solution containing the ion to be removed until the active sites in the exchanger are partially or completely "exhausted" by that ion. The exchanger may then be contacted with a sufficiently concentrated solution of the ion originally associated with it to "regenerate" it back to its original form.

The exchange reactions during "exhaustion" and "regeneration" can be represented by the following two reactions:

Exhaustion: $M^+X^- + R^-X^+ \rightleftarrows R^-M^+ + N^+ + X^-$ (6.1)

Regeneration: $R^-M^+ + N^+$ (high concentration)

$$\rightarrow R^-N^+ + M^+ \qquad (6.2)$$

In the first reaction, a cation exchange material designated R^-, having a cation N^+ associated with it reacts with a solution of an electrolyte (M^+X^-). In the regeneration reaction concentration of N^+ is higher than in the exhaustion reaction and the solution volume for regeneration is smaller, thereby making concentration of M^+ higher in the regeneration solution.

Regeneration of ion exchanger may also involve a third ion (for example a hydrogen ion in cation exchange) to give the corresponding form of the exchanger which can then be converted to the desired salt as shown below:

$R^-M^+ + H^+ \rightarrow R^-H^+ + M^+$ (6.3)

$R^-H^+ + N^+OH^- \rightarrow R^-N^+ + H_2O$ (6.4)

Such a sequence might be desirable in a case where H^+ was a much more effective regenerant than N^+ but where the release of H^+ into the solution being purified will be undesirable (Arthur D. Little, Inc., 1976).

Thus, during the process of ion exchange, undesirable ions from a stream are removed and transferred at a higher concentration to another aqueous stream.

The phenomenon of ion-exchange is known to occur with a number of natural solids (for example, soil, humus, metallic oxides, etc.) as well as synthetic resins which are presently used for most ion exchange applications.

6.3.1.1 Types of Ion Exchange Operations

Ion exchange operations are basically batch type but may be used on a semi-continuous basis. There are four operations carried out in a complete cycle, namely, service (exhaustion), backwash, regeneration, and rinse. There are three principal operating models in use today: concurrent fixed-bed, counter-current fixed bed, and continuous counter-current. Most ion exchange installations in use today are of the fixed bed type with counter-current operation becoming more popular, especially for removal of traces of hazardous species from the waste stream prior to reuse or discharge (Arthur D. Little, Inc., 1976).

6.3.1.2 Ion Exchange: State of the Art

One of the applications of the ion exchange process is in the metal-finishing industry for the recovery of chromic acid. The acidity of a chrome bath of average use is so high (pH 0.5 or less) that the use of any presently known cation exchange resin for direct removal of cations is impossible.

Also, the high oxidative potential of the waste results in rapid resin degradation of almost all available cation exchange resins (Raman and Carlson, 1977).

In a typical chromic acid recovery system, the acid rinse stream is first neutralized to a pH 8-9. Chromium (VI) is then removed by contact with a strong base ion exchanger (hydroxide form) and the resin is regenerated with a sodium hydroxide solution. The spent regeneration solution, which contains sodium chromate and sodium hydroxide, is neutralized with sulfuric acid and then treated with a cation exchanger to give chromic acid for recycle to the plating baths (Arthur D. Little, Inc., 1976). Hall, et al. (1979) quotes a study in which a chromic acid recovery efficiency of 99.5% has been demonstrated. Reduction in chromic acid purchases of 76-90% was also reported. Nitric acid can be recovered in a similar manner.

Recovery of valuable metals such as chromium, nickel, silver, and gold by ion exchange is more economically attractive than the conventional waste treatment processes (Fisher and McGarvey, 1967). A survey conducted by Plating and Surface Finishing journal (Anonymous, 1979) showed a favorable pay back for recovering nickel and gold with ion exchange equipment. It was reported that equipment cost payback of the chromium recovery units was not favorable because the equipment was old and not representative of current design for maximum efficiency.

Ion exchange is more attractive economically for the removal of heavy metals than the lighter ones when based on a weight basis, since the capacity of an ion exchanger is based on equivalent weight. For example, the weight of silver is 107 and of sodium 23, so that an exchanger can pick up four times the weight of silver compared to the weight of sodium it can hold (Gold and Calmon, 1980).

Another large scale application of the ion exchange process is the removal of aluminum from strong phosphoric acid/nitric acid solution used for cleaning ("bright dipping") aluminum metal (Skovronek and Stinson, 1977). The contaminated phosphoric acid is diluted with rinse tank water to give a 40% phosphoric acid solution which is then subjected to acid exchange to remove the aluminum. The purified phosphoric/nitric acid mixture is then evaporated to produce concentrated acid for recycle to the process. The resin is regenerated with sulfuric acid to give aluminum sulfate.

The ion exchange technique can be improved in terms of its utility and economics by using some ingenuity in design. For example, an ion exchange system, called "Reciprocating Flow Ion Exchange" has been perfected by Eco-Tec Limited for recovery of waste metals from plating operations (Brown, 1975).

There are a number of new developments in the areas of metal pickling waste treatment, cyanide removal, and novel ion exchange resins. A number of new ion exchange resins are being tested on a laboratory and pilot scale (Gold and Calmon, 1980). Many of these resins are of the macroreticular type and are less subject to fouling and loss of capacity than the older materials.

6.3.1.3 Limiting Technology

The ion exchange process is a well established process used in various industrial operations, however, the major limiting factor in applying this technique to new situations seems to be the presence of materials or conditions which may clog, attack, or foul the resins. For example, high concentrations of oxidizing agents such as nitric acid can damage the resins. Active research is currently being conducted to evaluate the use of new ion exchange materials, which would not be affected by the presence of such materials as mentioned above.

There seems to be a need for the development of highly basic anion exchangers which are stable at elevated temperatures when in the base form. Highly basic anion exchangers tend to foul with some surface waters and in solutions containing high molecular anionic species, therefore anionic exchangers less subject to fouling are needed which would increase applications in solutions containing foulants (Gold and Calmon, 1980).

More research is warranted to develop continuous ion exchange systems requiring less technical supervision and more controllability than those which exist.

In some cases the regenerant or eluting solution is not economically worth recovering or reusing. It can however become a pollutant if discarded into sewer lines or receiving waters. Therefore, more research is needed on full utilization of regenerants, higher regenerant efficiency, and reuse of regenerant effluents containing unused regenerant.

6.3.1.4 Recycle, Recovery, and Reuse Applications

The ion exchange process has been used for several years by different industries. Ion exchange is currently used for both general and selective removal of primarily inorganic ion species. Applications of ion exchange process in the waste treatment area include: treatment of a wide variety of dilute wastewaters from electroplating and other metal finishing operations, recovery of materials from the fertilizer manufacturing industry and hydrometallurgical processes, removal of cyanide from mixed waste streams, and recovery of chromium from cooling tower blowdown.

6.3.2 Reverse Osmosis

Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane, which impedes passage of solute but allows solvent flow (Weber, 1972). At a certain pressure exerted on the solution side of the membrane, called osmotic pressure, equilibrium is reached and the amount of solvent which passes in each direction is equal. If the pressure is increased above the osmotic pressure on the solution side of the membrane, the flow reverses. Pure solvent will then pass from the concentrated solution to the dilute solution. This is the underlying principle of the reverse osmosis.

The solvent flux (frequently expressed in gallons/ft^2-day) is given by (Arthur D. Little, Inc., 1976):

$$J = K\ (\Delta P)\pi \tag{6.5}$$

In which ΔP is the applied pressure, the osmotic pressure and K is a constant for the membrane-solvent system. As can be seen from this equation, the product-water flux rate decreases with increasing salinity (increasing osmotic pressure) of the feed solution.

The basic components of a reverse osmosis unit are the membrane, a membrane support structure, a containing vessel, and a high-pressure pump. Cellulose acetate and nylon are more common among the membrane materials used. The chemical nature of the membrane material is important because it affects the transport of solvent and rejection of solute. The membranes are susceptible to chemical attack and fouling and so pretreatment of certain feedwaters may be necessary to remove oxidizing materials. Usually, as a part of pretreatment, iron and manganese salts are removed to decrease scaling potential and the pH is adjusted to a range of 4.0 to 7.5 to inhibit scale formation.

6.3.2.1 Process Configurations

Based on the membrane support structure, reverse osmosis units may be classified under four categories: spiral-wound, tubular, plate and frame, and hollow fiber. The tubular configuration is recommended for use with domestic wastewater effluents while reverse osmosis system using a multitude of hollow nylon or polyamide fibers have shown considerable utility on commercial waste streams. Reverse osmosis units can be arranged either in parallel to provide adequate hydraulic capacity or in series to effect the defined degree of demineralization.

6.3.2.2 Reverse Osmosis: State of the Art

Research in the area of reverse osmosis has recently focused upon the development of improved families of membranes with increased flux, greater resistance to degradation in various liquid environments and improved rejection characteristics. Progress is also being made in recent years in improving mechanical designs for the modules, which can work efficiently with thin membranes at operating pressures of up to 800 psig (Leitner, 1973).

The effect of pH and temperature or membrane permeability was studied by Beder and Gillespie (1970). They reported that the flux rate was slightly higher under alkaline conditions. Their results also showed that a 5°C deviation from 25°C produced a 15% change in the membrane permeability constant, K. Similar results were reported by Wiley, et al. (1967).

Kojima and Tatsumi (1977), who studied the reverse osmosis treatment of wastewater from a chemical plant, reported that the performance of the membrance deteriorated gradually due to fouling and compaction of the membrane. It was found that the presence of organic matter, silica, calcium, and iron in the feed was responsible for the damage of the membrane. Pretreatment of the feed to reverse osmosis units is necessary for almost all industrial wastewaters. Due to the sensitivity of the membranes to the high concentrations of suspended solids in wastewaters, diatomaceous filters followed by a sand filter (Warnke, et al. 1976), or coagulation and sedimentation (Kojima and Tatsumi, 1977), have been used for pretreatment purposes. Removal of high concentrations of suspended solids in the feed before reverse osmosis is necessary in order to prevent clogging of the membrane and subsequent decrease in flux rates. Fouling of the membrane due to the presence of certain chemicals can be overcome by precipitating and filtering such materials by chemical treatment (Zabban and Helwick, 1980).

6.3.2.3 Statement of Limiting Technology

Reverse osmosis is a relatively new process and the development of this process has accelerated within the past few years, with a substantial increase in the number of commercial installations. There are, however, certain practical limitations to the use of reverse osmosis for waste recovery and reuse.

There seems to be a limitation on the pressures used in the reverse osmosis process. At high pressures, the membranes are subjected to compaction, which is accompanied by a decrease in product flux. Most units are limited to moderate temperature, acidic pH, and influent which can be prefiltered effectively to prevent fouling of membranes (Hall, et al. 1979).

The membranes available in the market at the present time are not sufficiently resistant to a wide range of chemicals, such as is often found in waste streams. These membranes do not seem to withstand extreme pH, temperature, and pressure. More research is needed to develop new membranes which will broaden the application of reverse osmosis.

Due to the limited applicability of the membranes, most of the industrial waste streams need some type of pretreatment prior to entering the reverse osmosis unit. Such pretreatment would, obviously, add to the overall cost of the treatment system and might pose a limitation to the use of reverse osmosis.

The waste stream from the reverse osmosis operation, in some cases, must be concentrated in an evaporator or subjected to some other treatment for a complete recovery of the pollutants. The limitations of reverse osmosis systems used in various industrial waste treatment operations are summarized in Table 1.

TABLE 6.1 EVALUATION OF RO FOR SYSTEMS TESTED (SKOVRONEK AND STINSON, 1977)

Attractive Systems	Limitations
Watts-Type Nickel	Boric acid selectively permeates membranes
Nickel Sulfamate	Boric acid selectively permeates membranes
Copper Pyrophosphate	Possible decomposition of pyrophosphate
Nickel Fluoborate	Boric acid selectively permeates membranes
Zinc Chloride	Need evaporation to close loop
Copper Cyanide	Need low-pH bath for current membranes:
Zinc Cyanide	Need low-pH bath for current membranes: need evaporation to close loop
Cadmium Cyanide	Need low-pH bath for current membranes: need evaporation to close loop
Unattractive Systems	**Limitations**
Chromic Acid	Attacks and destroys all membranes unless neutralized
Very-high pH Cyanide Baths	Attacks and destroys all membranes commercially available: newer membranes under development show promise for treating high-pH cyanide baths

6.3.2.4 Recycle, Recovery, and Reuse Applications

Reverse osmosis is gaining importance as an industrial unit operation only in recent years. Initially, it was used for production of potable water, however, it is currently used in a broad spectrum of industrial operations. Recent research indicates wastewater reclamation by reverse osmosis offers great promise for substantial reductions in cost as well as marked improvements in pollutant removal efficiency.

Reverse osmosis has been used for various industrial operations and its use is expected to expand as its utility is demonstrated and its technology becomes more familiar to its potential users. Some of the applications of reverse osmosis in waste treatment area include: plating wastes, paper mill effluents, laundry wastewaters, food processing wastes, acid mine drainage waters, and petrochemical wastewaters.

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CHAPTER 7

SECTION II

PHASE TRANSITION

7.1 INTRODUCTION

Processes of heat transfer accompanied by phase changes are more complex than simple heat exchange between fluids. A phase change involves the addition or subtraction of considerable quantities of thermal energy at constant or nearly constant temperature. In Chapter 7, four processes will be examined which rely on one (or several) constituents of a wastestream to undergo a phase change in order to separate it (and in many cases these constituents are recycled and reused) from the main fluid stream. The processes to be examined include:

1. Condensation
2. Distillation
3. Evaporation
4. Refrigeration

Condensation, evaporation and refrigeration are processes used primarily to separate the constituents of a wastestream. Once separated, these constituents can be further purified and either recycled back into the process or sold. Evaporation, on the other hand, is basically used to concentrate a non-volatile solute by vaporizing the volatile solvent. The solvent, can then be condensed, purified and recycled into the process for further use. The concentrate (non-volatile solute and remaining solvent) can also be recycled or disposed of at this point.

For each of the four listed processes, a brief process description will be provided. Also, a review of the current recycle, recovery, and reuse applications will be given as well as a statement on the processes limiting technology.

7.2 CONDENSATION

In a two component vapor containing one condensable and one noncondensable component, condensation will occur when the partial pressure of the condensable component equals that component's vapor pressure. This may be effected in one of two ways: The system pressure may be increased at a given temperature until the partial pressure of the condensable component equals its vapor pressure. Alternately, and far more commonly, the pressure remains fixed and the temperature of the mixture is reduced to the point where the vapor pressure of the condensible component equals its partial pressure. At further reduction in temperature, condensation continues such that the partial pressure is always equal to the vapor pressure (Anonymous, 1978).

Condensers may employ contact or non-contact methods for cooling the vapor. Contact condensers usually spray an ambient temperature or slightly chilled water or other liquid directly into the gas stream in order to condense the vapor. The contact condenser may also act as an absorptive system, scrubbing vapors which might not be condensed, but which are soluble in the liquid. Because the temperature approach between the liquid and the vapor is very small, condenser efficiency is high. Large volumes of liquids are required, however.

Direct contact condensers are seldom used for the removal of organic solvent vapors because the condensate will contain an organic-water mixture which must be separated or treated before disposal. They are effective in cases where it is necessary to remove heat from hot gas streams without concern for recovery of organics. Spray towers, high velocity jets, and barometric condensers are among the equipment used for contact condensation.

In practice, crude empirical correlations are usually used in designing and predicting performance of a contact unit (Theodore, and Buonicore, 1975).

Surface condensers are non-contact units which may also be referred to as heat exchangers. A common surface condenser is the shell-and tube heat exchanger in which the coolant flows through the tubes and vapor condenses on the outer tube surface. The film of condensed vapor which develops drains away to storage or disposal. In this way, the coolant contacts neither the vapor nor the condensate. Surface condensers may also be air-cooled. These air-cooled units usually have extended surface fins; vapor condenses within the finned tubes (Theodore and Buonicore, 1978).

Although contact condensers are generally less expensive, easier to maintain, more flexible, and more efficient in removing organic vapors than surface condensers, surface condensers are more attractive with respect to recovery of marketable condensate and a minimal waste disposal problem (Anonymous, 1978). Furthermore, water used as a surface condenser coolant may be reused, and surface condensers produce 10 to 20 times less condensate than do contact condensers (Theodore and Buonicore, 1978). Because high removal efficiencies are not obtainable with low condensable vapor concentrations, condensers are typically used when the vapor concentration in the stream to be treated is high, and are often located upstream of after burners, carbon beds, or absorbers as a pretreatment measure.

7.2.1 Limiting Technology

High removal efficiencies are not obtainable with low concentrations of condensable vapors. This limits the application of the condensation process to streams having a high vapor concentration or to pretreatment of streams fed to after burners, carbon beds or absorbers.

A shell and tube heat exchanger installed on a neoprene monomer isomerization tower was installed to treat a total waste gas flow of 331 lb/hr. The hydrocarbon waste gas flow was 159 lb/hr. The exchanger, cooled by -2°F brine solution, condensed 81% of the contained hydrocarbon with an energy requirement of 22,000 Btu/hr. The recovered hydrocarbons were returned to the process for utilization (Pruessner and Broz, 1977).

In a process in which fuels are produced from coal, volatile products released from the coal in fluidized bed reactors pass to a product recovery system for recovering the oil and cooling the gases. The coal-oil vapors are directly contacted with a water-rich stream for condensation. The oil-phase is dehydrated and filtered to remove solids before being pumped up to pressure and mixed with hydrogen for hydrotreating in a fixed-bed catalytic reactor. Hydrotreating removes sulfur, nitrogen, and oxygen to produce a synthetic crude oil (Jones, 1974).

Power plant turbine exhaust steam has been mixed with cooling water in a direct contact condenser maintained under a vacuum. The temperature of the water is less than the boiling temperature under the vacuum conditions in the condenser. The mixture of cooling water and condensed turbine exhaust is divided such that one portion is sent to the boiler, suitable for use in generating steam to drive the turbine, while the other portion is sent to the condenser for use as cooling water after it has passed through an air cooled heat exchanger. Water to be used for cooling is placed in the heat exchanger with liquid gaseous fuel so that the fuel is vaporized at the expense of heat lost from the water (Anonymous, 1974).

In work on liquid fuel synthesis using nuclear power in a mobile energy system, Steinberg and Beller proposed to extract CO_2 from the atmosphere by compressing air, condensing the water from it, drying the resultant air with a molecular sieve, and extracting CO_2 by another molecular sieve (Steinberg and Beller, 1964). Williams and Campagne (1971), however, found compressor costs for such an operation to be prohibitive.

At a neoprene polymer plant where neoprene latex is manufactured in batch reactors, each charging and emptying of a polymerization reactor causes displacement of some waste gas. Collected waste gas is discharged to a direct contact cooler. A problem which precluded the use of a shell and tube exchanger was the regular carryover of latex to the collection system, anticipated to produce a high rate of fouling. The waste gas flow of 275 lb/hr, containing about 125 lb/hr hydrocarbon contamination, is cooled with chilled water resulting in the condensation of 43% of the hydrocarbon. Exit gas from the direct contact cooler is treated in an absorption system

The absorption system consists of a five-stage oil absorption tower. An overall efficiency of the contact cooler/absorption system exceeds 98% hydrocarbon removal. The recovered hydrocarbon is stripped from the oil and returned to the manufacturing process for further use. The installed cost of the system amounted to $300 (Pruessner and Broz, 1977).

A solvent recovery system features an inert nitrogen atmosphere in an oven/dryer process. In this process, resin curing is accomplished by evaporating the organic solvent in which the resin is dissolved. This eliminates the requirement for oven ventilation with atmospheric air normally required to dilute solvent concentrations to below-explosive levels. By using the inert nitrogen atmosphere, solvent vapor can be safely concentrated to well above traditional oven levels. At these levels, the solvent is recoverable by condensation. According to the manufacturer, solvent recovery is about 99%, and overall fuel requirements are reduced by 40% (Anonymous, 1980).

7.3 DISTILLATION

Distillation is a unit operation employed by industry for the separation, segregation, or purification of liquid organic product streams, some of which may contain aqueous fractions. The term distillation is properly applied only to those operations in which vaporization of a liquid mixture yields a vapor phase containing more than one component. This distinguishes the process from that of evaporation.

As a unit operation, distillation has been successfully used either singly or in combination with such operations as direct condensation, adsorption, and absorption for the recovery of organic solvents. With regulations which are becoming increasingly stringent for air pollution control, liquid effluents, land site disposal, and the rising cost of organic chemicals, distillation should become more competitive with other methods of organic liquid recovery and disposal.

The practical limitations of the process are economic in nature; both operational and equipment costs are high. The difficulty in separating the contents in the liquid to be distilled defines the economic and energy requirements of the process (Berkowitz, et al. 1976).

Theoretically, distillation can generate products of 100% purity. Physical parameter restrictions such as entrainment effects limit the degree of attainable purity to the 10^{-9} to 10^{-14} range of impurities, however. Usually, the attainment of these limits is not necessary.

In terms of the physical separation of liquid components, there are no limitations in feed composition or in reaching the desired composition in any of the product streams. To avoid plugging of equipment or costly maintenance problems, however, it is preferred that the materials to be distilled do not contain appreciable quantities of solids or non-volatile materials, and that the feed does not have a tendency to polymerize. If it is known that feeds of a "dirty" nature must be handled, pretreatment steps employing filtration, thin-film evaporation, scrubbers, electrostatic precipitators, or cyclones may be taken. When pretreatment is not possible, specially designed equipment may be required.

7.3.1 Types of Distillation Processes

The most common types of distillation are those of batch and continuous fractional distillation. Certain feed streams require more specialized processing, however.

When it is necessary to distill an azeotrope, pressure or vacuum may be applied to shift the azeotropic composition. More often, an additive is introduced to the mixture to form a new boiling point azeotrope with one of the original constituents. The volatility of the new azeotrope is such that it may be easily separated from other original constituents.

Binary mixtures which are difficult or impossible to separate may also be distilled by extractive distillation. In this process, a solvent is added to the mixture which alters the relative volatility of the original constituents, thus permitting separation. The added solvent is of low volatility and not appreciably vaporized.

In the case of a heat sensitive feed stream, molecular distillation may be used. This process is conducted at absolute pressures on the order of 0.003 mm of mercury (Berkowitz, et al. 1976).

7.3.2 Limiting Technology

Theoretically, distillation can generate products of absolute purity. Entrainment effects limit the degree of attainable purity to the 10^{-9} to 10^{-14}

range. This level of purity is rarely required.

The presence of formation of solids or non-volatile material in the feed stream is undesirable due to operating difficulties which they may cause. In cases where such materials are present, pretreatment steps such as filtration are necessary to minimize the plugging of distillation equipment or costly maintenance problems.

In some distillations, solvents may be added which alter the volatility of a binary mixture which is difficult to separate. Further study of additives which produce this beneficial effect may be useful.

The fact that the distillation process is energy intensive tends to limit its application, but with increases in by-product recovery credits, it may become competitive with more commonly utilized processes.

Organic peroxides, pyrophoric organics, and inorganic wastes cannot generally be treated by distillation.

7.3.3 Recycle, Recovery, and Reuse Applications

Typical industrial wastes which can be handled by distillation include:

- Plating wastes containing an organic component - usually the solvents are evaporated and the organic vapors distilled.
- Organic effluents from printed circuit boards are adsorbed on activated carbon. Regeneration of the activated carbon gives a liquid which is distillable for recovery of the organic component.
- Phenol recovery from aqueous solutions is a major waste treatment problem. The recovery process uses a polymeric adsorber. The adsorber is

regenerated using a vaporized organic solvent. A complex distillation system is used to recover both the regeneration solvent and the phenol.

- Methylene chloride which contains contaminants is a disposal problem, but it can be salvaged for industrial application by distilling.
- Methylene chloride can be recovered from poly urethane waste.
- The separation of ethylbenzene from styrene and recovery of both.
- Waste solvents for reuse in cleaning industrial equipment. Usually a mixture of acetone (ketones) (alcohols) and some aromatics (Berkowitz, et al. 1978).

7.4 EVAPORATION

Evaporation is the vaporization of a liquid from a solution or a slurry for separation of liquid from a dissolved or suspended solid or liquid. The basic principle underlying evaporation is to concentrate a solution consisting of a non-volatile solute and a volatile solvent (Arthur D. Little, Inc., 1976). This is usually achieved by condensation of steam on metal tubes, which have the material to be evaporated flowing inside them. The solvent, which is in a vaporized form after the evaporation process, may be discharged as an exhaust or can be condensed, purified, if necessary, and reused. Similarly, the residue from the evaporation process, which is called the concentrate, can be disposed of or the useful materials in it may be reused. A typical example where both the condensate and the concentrate can be recycled back to the original process where these materials are used is the electroplating industry.

7.4.1 Process Configurations

Basically, there are two types of evaporation systems, namely atmospheric evaporation and vacuum evaporation. Atmospheric evaporation can be accomplished simply by boiling the liquid. Evaporation can be achieved at lower temperatures by spraying the heated liquid on a surface and blowing air over the same surface.

In vacuum evaporators, the boiling temperature is reduced by lowering the evaporating pressure. The water vapor is condensed and the non-condensible gases are removed by a vacuum pump. Vacuum evaporation may be either single or multiple effect.

Single effect evaporators are used where the required capacity is small, steam is cheap, the vapors on the liquids are so corrosive that very expensive materials of construction are required, or when the vapor is so contaminated that it cannot be reused (Arthur D. Little, Inc., 1976).
In a multiple-effect evaporator, steam from an outside source is condensed in the heating element of the first effect. The vapor produced in the first effect is used as the heating medium of the second effect, which is operating at a lower pressure than the first effect. The vapor from the second effect is used as the heating medium for the third, and so on. Each consecutive effect operates at a lower pressure than the preceding effect.

Several types of evaporators are used for the separation and recovery of different organic and inorganic compounds. In process industries, such as metal and plastics finishing industries and particularly the electroplating industry, closed-loop recycling of wastes is achieved by using evaporation as a recovery process. In a closed-loop system, the condensate and the concentrate are recycled back to the rinsing and plating operations respectively, thereby forming a closed-loop treatment.

7.4.2 Evaporation: State of the Art

A survey done by Plating and Surface Finishing journal (Anonymous, 1979) concluded that a favorable payback for evaporative equipment is achieved for the recovery of chromium, nickel, and lead-tin alloy plating chemicals but not for zinc cyanide solutions. It was felt that operating costs for recovery equipment exceeded the saving in zinc plating chemicals. However, recovery may be justified because it eliminates costly cyanide destruction, zinc precipitation, and solids separation. There does not seem to be much information available in this area and more research is needed to study the application and cost analysis of evaporation systems for recovering zinc plating chemicals.

Recovery of industrial pollutants by evaporative techniques becomes more cost-effective when the pollutants in the wastes are in high concentrations and the flow rates are low. In order to achieve this, multistate countercurrent rinse tanks are suggested in the case of the electroplating industry.

As mentioned earlier, one of the major limitations of evaporation techniques is the cost of heating from steam generators. This may be substantially reduced by utilizing waste heat from the plating baths of the electrochemical industry (Cheremisnoff, et al. 1977; Hall, et al. 1979; Skornonek and Stinson, 1977). More research is warranted in this area to determine the feasibility and economics of utilization of waste heat.

Another way to economize on energy consumption is to use multiple-effect evaporation technique, in which the vapor produced from one effect is used as the heating medium for the next one. In fact, one electroplating company abandoned its use of a single-effect evaporator for nickel recovery because operational costs were greater than the value of the recovered nickel and calcium ions and other impurities resulted in the clogging of anode bags. This company now uses three counter-flow rinses to concentrate and recover nickel salts from its rinse water waste and periodically dumps the fourth final rinse to control impurities (Anonymous, 1979).

In the case of cyanide copper plating operations, certain types of evaporation techniques (for example, climbing film evaporators), may not be used since the materials of construction in use are appropriate only for acid pH. Different types of materials are needed in such cases (Hall, et al. 1979).

7.4.3 Process Modifications

Ideally, evaporation results in a concentrate and a deionized condensate. But in a practical situation carry over of some impurities in the condensate may occur. Furthermore, the concentrate may also contain organic brighteners and anti-foaming agents. An activated carbon bed may be necessary to remove such impurities before the condensate is recycled back (Hall, et al., 1979). Similarly, impurities may be found in the concentrate, which can also be purified by several types of treatments.

In order to recover copper from copper cyanide plating operations, the concentrate may be treated with peroxide, caustic potash, and activated carbon (Hall, et al. 1979).

In the case of nickel plating operations, (Atimion, 1980) reported that when the nickel solution is sufficiently concentrated from evaporation, it is pumped from the evaporator to a stainless steel tank for carbon treatment at pH 1.5 to 1.7. The solution is then filtered into a clean tank and nickel carbonate is added to the solution to raise the pH to 5.0 to 5.5. Then required doses of potassium permanganate and activated carbon are added to remove sulfur. After settling for eight hours, the treated solution is filtered twice and recycled to the plating bath.

Pretreatment of the wastewater is sometimes necessary to make the evaporation process applicable to a given situation. For example, most of the companies using evaporators to recover chromium solution have installed cation exchangers to control the concentration of trivalent chromium and other metallic impurities that tend to reduce cathode efficiency on the plating (current density) range (Anonymous, 1979; Hall, et al. 1979; Kolesar, 1972; Cheremisnoff, et al. 1977). In the case of cyanide plating, purification is accomplished by precipitation of carbonate, which is best done at the point of maximum concentration (Cheremisinoff, et al. 1977).

7.4.4 Limiting Technology

There do not seem to be any fundamental limitations on the applicability of evaporation process, however, energy consumption appears to be the major obstacle. There are certain practical limitations in the application of evaporators. In addition to heat transfer characteristics and economic energy utilization, the other variables that limit the practical application of evaporation process are crystal formation, salting, scaling, corrosion entrainment, and foaming (Arthur D. Little, Inc., 1976).

In order to prevent these problems in evaporators, studies should be conducted to determine the proper type of evaporation for a given industrial operation. Information in this area seems to be scarce.

It seems that most of the work on application of evaporation techniques used for the recovery of industrial pollutants has been done in the electroplating industry. Evaporation systems are also used by the paper industry to recover the chemicals from the Kraft pulping process (Arthur D. Little, Inc., 1976). More research needs to be done to determine the applicability of evaporation techniques for recovery of inorganic compounds in other industries.

7.4.5 Recycle, Recovery, and Reuse Applications

Evaporation is a well-defined and well-established process that has been used in several industrial operations for a number of years. There probably is no chemical industry at this time which does not use evaporation systems of one kind or another. The evaporation process is used for a variety of purposes including dehydration, crystallization, separation, concentration, and recovery of various industrial chemicals.

7.5 REFRIGERATION

The production of cooling, or heat withdrawal, may be accomplished by the solution, melting or evaporation of a substance, or by the extension of a gas. The term refrigeration refers particularly to cooling below atmospheric temperature. Machines which produce cooling may be classified into compression and adsorption refrigeration machines, depending on the mode of recovery and circulation of material.

Compression refrigeration machines evaporate low-boiling liquids and condense their vapors or gases. Mechanical energy is used to effect compression of the refrigerant, following compression, where it becomes liquefied through heat transfer. The refrigerant is then sent from the condensor to the evaporator where it withdraws heat by evaporation and is recycled for compression. Electric energy may also be used to compress the refrigerant and turbo-compressors driven by electric motors or steam turbines may be used instead of piston compressors.

Adsorption refrigerating machines utilize heat to produce cold, and operate economically when waste heat is available. They are especially useful for low temperature evaporation pressures. Refrigerant leaving the evaporator travels to an adsorber where it is bound by the aid of a liquid pump. After passing through a heat exchange, it travels to a stripping tower, where the refrigerant is stripped from the water by the addition of heat. The gas is then liquefied in the condensor. The mechanical compressor used in compression refrigerating machines is substituted by a thermal compressor in adsorption refrigerating machines (Perry, 1963).

In practice, vapors undergoing refrigeration are condensed by either contacting a cold surface or by contact with the coolant. When a vapor is refrigerated for the purpose of emission control of product recovery, the unit in which heat transfer takes place between the refrigerant and the vapor is referred to as the condensor. In a surface condensor, the coolant does not contact the vapors or condensate. Coolant, vapors and condensate are intimately mixed in contact condensors.

The choice of condensor will be influenced by a) the presence of moisture with the vapor, b) the operating temperature level and c) whether or not the condensed vapors are to be reused as product liquid. Cooling an air-vapor stream condenses the moisture to liquid at temperature above 32° F. This may lead to a gradual build up of frost which can be removed by scrapers or by periodically raising the surface temperature above 32° F. A contact condensor does not lend itself to frost removal, since any solid which is formed circulates with the contact and condensate, impairing the performance of pumps and valves (Honegger, 1979).

7.5.1 Limiting Technology

In the case of hydrocarbon recovery, removal efficiency by refrigeration depends on the hydrocarbon concentration of inlet vapors.

The degree of produce recovery by refrigeration is also dependent on the refrigeration temperature level. The more volatile the product, the lower the temperature required for effective recovery. When moisture is entrailed in the vapor, special equipment may be necessary to accommodate the ice and frost which build up, impairing process performance.

7.5.2 Recycle, Recovery, and Reuse Applications

Refrigeration is one of several competing methods for recovering emissions from bulk liquid transfer and storage operations, and has been promoted for vapor recovery at gasoline loading racks. Equipment and operating costs are relatively high for this application because ultra-low temperatures are required for effective recovery (Honegger, 1979).

At some gasoline terminals, vapors are compressed and then refrigerated to obtain condensation. Other installations omit compression and refrigerate the vapors to temperature approaching 73° C (100° F). Removal efficiencies depend on the hydrocarbon concentration of inlet vapors. In the case of saturated hydrocarbons, removals of greater than 96 percent are possible. Similar systems have been proposed for marine petroleum terminals (Anonymous, 1978).

The degree of product recovery is also dependent on the refrigeration temperature level. The more volatile the product, the lower the temperature required for effective recovery. Since many hydrocarbon vapors require temperatures below the point at which water freezes, special equipment may be necessary to accommodate the ice and frost which form due to moisture entrained in the air (Honegger, 1979).

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CHAPTER 8

SECTION II

CHEMICAL MODIFICATIONS

8.1 INTRODUCTION

Chapter 8 of this report examines several chemical treatment processes currently being used to recover heavy metals from industrial sludges and wastewaters. The processes to be discussed include:

1. Cementation
2. Precipitation
3. Catalytic Hydrogenation
4. Reduction

For each of the above listed processes, the following areas will be discussed:

1. Process Description
2. Recycle, Recovery, Reuse and Applications
3. Statement of Limiting Technology.

The "Recycle, Recovery and Reuse Applications" section will discuss the past and current work using each process in the recovery of heavy metals from industrial wastewaters. The "Limiting Technology" section discusses the advantages, disadvantages and limitations of each process in its application of removing as well as recovering the metals.

8.2 CEMENTATION

Cementation is the recovery of an ionized metal in solution by spontaneous electrochemical reaction to its elemental state through the oxidation of another elemental metal which is also kept in solution. The process can be predicted in terms of electrode potentials. The metal with more positive oxidation potential in the electromotive series will pass into solution displacing a metal with a less positive potential. Since, in electrodeposition, the less noble metal goes into solution, scrap iron is often chosen as the reductant because of its low cost.

The cementation process is commonly used to recover copper tailings. Streams bearing copper ions are passed through a series of reaction tanks containing scrap iron, where the copper is removed as elemental metal and the iron is displaced into solution. The reaction is as follows:

$$Cu^{+2} + Fe^{0} \rightleftarrows Cu^{0} + Fe^{+2} \qquad (8.1)$$

The cementation process generates electrodeposits without external current. For example, an electropotential sufficiently large to deposit copper is produced when copper ions and iron surface are present in the aqueous solution.

The process can be described as a galvanic corrosion cell. A cathodic copper deposit covers the anode except for sub-microscopic regions from which iron is being the basic metal, in the manner of a short-circuited galvanic cell. These anodic sites effectively migrate around the surface of the iron; therefore the entire piece of iron can be consumed. The copper deposits can be stripped from the surface of the iron through vigorous stirring or agitation and the resulting copper sludge can be carried as high purity copper (Patterson and Jancuk, 1977). Iron is less toxic than copper and can be readily oxidized by air and removed from solution.

If hexavalent chromium is also present along with copper in the wastewater, during the process of cementation, the former may react with either elemented on ferrous iron to yield trivalent chromium (Jester and Taylor, 1973).

$$2\,Cr^{+6} + 3Fe^{0} \rightarrow 2Cr^{+3} + 3Fe^{+2} \qquad (8.2)$$

$$Cr^{+6} + 3Fe^{+2} \rightarrow Cr^{+3} + 3Fe^{+3} \qquad (8.3)$$

8.2.1 Limiting Technology

The cementation process has been proven to be effective for the removal and recovery of copper from waste streams of small flow. It has not been exploited for larger flows due probably to the need for longer contact time with the metallic interface.

There seems to be an excess iron consumption (i.e., more than needed on the basis of stoichiometry) associated with the process due to some side reactions of iron in the wastewater. Disadvantages of excess iron consumption include wastage of the metallic iron reactant and production of unnecessary amounts of iron sludge upon precipitation treatment.

Thermodynamic limitations and the need for process optimization seem to prevent the removal of copper to the low levels required in most effluents. Therefore the residual copper levels after cementation treatment would normally require additional costs to the overall treatment.

The cementation process for recovery of metals seems to be in an infant stage and needs to be studied more.

8.2.2 Recycle, Recovery, and Reuse Applications

The cementation process is employed to a very limited extent by industry today. The hydrometallurgical industry employs the cementation process for the recovery of such metals as copper on iron, silver and gold on zinc, lead on iron or zinc, palladium on copper, thallium on zinc, gold from gold chloride on cadmium, and gallium on aluminum (Habashi, 1970).

A few industries have set up wastewater treatment operations for chromium reduction and copper recovery using the cementation process. The Anaconda American Brass Company utilized the cementation process as outlined by their patent for copper recovery. The copper sludge from their treatment plant contained 30-40% moisture with 70-80% elemental copper on a dry basis.

The Scovill Manufacturing Company in Waterbury, Connecticut adapted the Anaconda approach and designed a process for a simultaneous chroming reduction and copper removal (Jester and Taylor, 1973). The copper sludge from this operation contained more than 90% elemental copper by dry weight.

Other known applications of cementation include copper recovery from water pickle liquor in a brass mill (Dean, et al., 1972), and the reduction of cobalt and vanadium with iron metal in the treatment of waste ammonium, persulfate etching solutions (E. M. Songio, cited in Jancuk, 1976).

Industrial application of cementation process for copper recovery produced a mud of about 30-40% moisture, with the dry weight analysis of 95-99% (Keyes, 1966), 70-80% (Jester and Taylor, 1973; Case, 1975) pure copper.

8.3 PRECIPITATION

Chemical precipitation is the most common method for removal of inorganic heavy metals found in industrial waste effluents. Precipitation of a heavy metal ion occurs when the salt with which it is in equilibrium reaches its solubility limit, as defined by its solubility product. The value of the logarithm of the solubility products of different metal salts are available in the literature (Bard, 1966; Feitknecht and Schindler, 1963; Martell and Smith, 1974a, 1974b, 1974c, Sillen and Martell, 1964, 1974). These constants may be used to plot the theoretical solubility diagrams for each metal which can be used for determining the pH levels at which each metal is least soluble. An example of such diagrams is shown in Figure 1.1 for various metals as hydroxides in pure water.

Theoretical solubility diagrams such as those shown in Figure 1.1 can be used only as approximations for determining the pH levels at which each metal can be precipitated in the greatest quantity as a given salt, since the solubility of metals may vary in aqueous solutions depending upon temperature, ionic strength, and the presence of anions or other complexing agents in solution (Butler, 1964; Stumm and Morgan, 1970).

Most of the inorganic heavy metals generally found in industrial waste effluents are removed by precipitation as hydroxides. The process of precipitation involves the adjustment of pH of the waste stream by addition of an acid or an alkali, and coagulating to effectively remove the resultant hydroxide through classification and/or filtration. Metals may also be removed by precipitation as sulfides. Metal sulfides are generally more insoluble in water systems than corresponding hydroxides. However, one of the limitations of sulfide precipitation is that sulfides can hydrolyze to form extremely noxious hydrogen sulfide gas.

Chemical precipitation of heavy metals may be accomplished by other batch or continuous treatment systems. Equalization of the waste stream may be necessary for continuous systems if the flow and pH of the waste vary widely with time. The first process step is the adjustment of the pH by addition of acid or alkali to achieve the defined pH level for optimum precipitation. A polymer is usually added to aid coagulation. The waste stream then flows into a sedimentation tank, where the heavy metal precipitate settles out. Precipitated sludge may be recirculated to the precipitation tank in order to provide a seed which will aid agglomeration of the newly formed precipitate.

The chemicals most frequently used for precipitation of metals are lime, caustic soda and sodium carbonate. Lime is preferred because of its relatively lower cost, caustic is used in small installations where daily chemical costs are not significant, and soda ash is used in cases where it provides a batch chemical reaction (e.g. cadmium and nickel precipitation) (Lanouette, 1977).

8.3.1 Limiting Technology

Although the solubility of many metallic compounds is extremely low in pure water, such levels can not be achieved in industrial effluents after precipitation processes, because of the presence of complexing agents, which tie the metals in solution. Furthermore, when two or more metals are found in the same waste stream, the problem becomes even more complex, since the optimum pH for precipitation may be different for each ion. The question then becomes whether to treat the waste at a pH which would produce satisfactory, but not optimum results for each of the metal ions present in the wastewater, or to treat it at the optimum pH for one metal ion, remove that metal precipitate, and then treat for the second metal ion and so forth.

8.3.2 Recycle, Recovery, and Reuse Applications

The precipitation process is used in full-scale treatment of many industrial wastewaters containing heavy metals. Wastewater streams from the iron and steel industry (USEPA, 1974), metal finishing industry, (FWDA, 1968) and inorganic chemical industry (USEPA, 1975) are some typical examples which receive precipitation treatment for removal of heavy metals.

Cadmium, generated in effluents from pigment works, textile plants, is usually removed by hydroxide precipitation. The optimum pH for cadmium hydroxide precipitation is around 11. Such high pH treatment would require lowering the pH of the final effluent in order to meet effluent standards. Since this pH adjustment will redissolve any remaining cadmium, it is essential that the metal precipitate is removed effectively by filtration for sedimentation. Due to the high value of cadmium, the precipitated sludge may be sent to a reprocessor for recovery of cadmium.

Chromium is found in either hexavalent or trivalent form. Hexavalent chromium is found in the waste streams of plating operations, aluminum anodizing, and paint and dye operations, while trivalent chromium is common in effluents from the photographic, ceramic, and glass industries (Lanouette, 1977). Treatment for chromium usually consists of reduction of hexavalent chromium to its trivalent form and precipitation of the trivalent chromium by addition of lime or caustic to increase the pH to between 7.5 and 8.5, where minimum solubility of chromium hydroxide occurs.

Lead which is found in waste effluents from battery manufacture, and printing, painting and dyeing operations can be precipitated with lime or caustic soda to form lead hydroxide; with soda ash to form lead carbonate; or with trisodium phosphate to form lead phosphate.

The standard method of removing mercury is to adjust the pH to 5 to 6 with H_2SO_4 and then add sodium sulfide to an excess of 1-3 mg/l. This forms an insoluble mercury sulfide, from which the metal can be recovered.

8.4 CATALYTIC HYDROGENATION

Catalytic hydrogenation is a useful method for achieving controlled transformation or organic compounds. The reaction is carried out easily and produces high yield of a product free of contaminating reagents. Satisfactory results can often be obtained over a wide range of conditions of temperature, pressure, and degree of agitation, factors which can affect both activity and selectivity in catalytic hydrogenation.

In any liquid phase hydrogenation, hydrogen moves from the gas phase across a gas-liquid interface and from the liquid phase across a liquid-solid interface to the external surface of the catalyst and then into its porous structure. The net movement of hydrogen to the catalyst results from concentration gradients which develop when hydrogen is consumed by the catalytic reaction. In many cases the reaction rate is limited wholly or partially by the speed with which hydrogen is transported to the catalyst surface. Mass transport is more likely to become a limiting factor as a catalytic activity increases.

Due to mass transport limitations on the rate of hydrogenation, hydrogen availability at the catalyst surface may vary from a condition in which the rate of reaction is controlled almost entirely by the rate of chemical reaction to one in which the rate is controlled completely by the rate of hydrogen transport to the active catalyst site.

The process of hydrogenation takes place in a reaction which brings hydrogen, the catalyst, and the substrate into contact in the absence of air. Most hydrogenations are carried out in batch-type reactors, although in some cases, especially large-scale processes, continuous reactors are used. Reactors may be built for hydrogenation at atmospheric pressure, low pressure, and high pressure. Fixed-bed reactors are useful in the hydrogenation of large volumes of material, and may take the form of a trickle bed, in which a liquid phase and hydrogen flow concurrently downward over a fixed bed of catalyst particles, or a flooded bed, in which hydrogen and the liquid pass concurrently upward.

Hydrogenation catalysts differ widely in activity and selectivity, with these characteristics determined mainly by the major metal component. Metals can be ordered into a hierarchy of activity for hydrogenation of each functional group. Noble metal batch-type catalysts usually contain between 1 and 10% metal; fixed-bed catalysts usually contain 0.11.0%. On a weight of metal basis, activity is linear with metal concentration over a limited range. As metal concentration increases, metal becomes piled upon metal, making an increasing percentage unavailable for use. On a weight of metal basis, the more dilute the metal, the more efficient the catalyst, but the amount of catalyst (metal plus support) needed to maintain a constant weight of metal increases directly as the metal concentration decreases. A compromise is made between making the most efficient use of metal and the economic need to minimize the amount of catalyst used. Supported base metal catalysts usually contain much more metal than noble metal catalysts.

Two catalysts used in combination may sometimes give better results than either used separately. Synergism has been explained by the assumption that hydrogenation involves multiple intermediates, some of which may be reduced more easily by one catalyst and some by the other. The second catalyst may also function by its superior ability to remove catalyst inhibitors formed in the reaction.

Catalyst poisons vary from reaction to reaction. Poisons included heavy metal cations, halides, divalent sulfur compounds, carbon monoxide, amines, phosphines, and in some cases, the substrate itself or some product of the reaction. Small amounts of a certain substance may be beneficial to catalyst functioning, while larger amounts will be poisonous. A quantitative measure of catalyst poisons can be made by carrying out the same hydrogenation at different catalyst loadings. If the rate increases more rapidly than the increase in amount of catalyst, the presence of a poison is confirmed.

Small quantities of various substances which favorably affect catalyst life, activity, or selectivity may be termed promoters. The effect a promoter may have also depends on the reaction which the catalyst is used. There is little theory on which to base the use of promoters, and their successful use usually proceeds from an extension or modification of something already known.

Heterogeneous hydrogenation catalysts may be either supported or unsupported, the former type being further divided into those for use in slurry processes and those for use in fixed bed operations. Catalysts used in slurry processes are usually fine powders, while fixed-bed catalysts are usually in the form of cylinders, spheres, or granules. A good carbon or alumina will be suitable as a catalyst support for the majority of reactions.

Solvents may be used to increase ease of handling and catalyst recovery, to moderate exothermic reactions, increase rate and selectivity, and permit hydrogenation of solid material. Most liquids which are stable under hydrogenation conditions and which do not inactivate the catalyst can be used as solvents. Commonly used solvents include acetic acid, methanol, and ethanol.

A problem which may arise during the hydrogenation process is the agglomeration of the catalyst. This will have an adverse effect on the rate and may even cause the reduction to fail. Agglomeration can often be overcome by changing the pH of the medium or by changing the solvent, the solvent-substrate ratio, or the catalyst support.

Lost catalytic activity may in some cases be restored by regeneration. Regeneration techniques are basically a variation or combination of oxidations, hydrogenation, steaming, heating, or solvent wash. It is difficult to predict in advance which procedures will work. Eventually, a catalyst can no longer be sufficiently regenerated. Noble metal catalysts can then be returned to a refiner and destroyed, if volume warrants, for subsequent recovery of the pure metal. Base metals may or may not be reclaimed (Rylander, 1972).

8.4.1 Limiting Technology

Catalytic hydrogenation is a useful method for achieving controlled transformation of organic compounds.

Due to mass transport limitations on the rate of hydrogenation, it may vary from a condition in which it is almost entirely controlled by the rate of chemical reaction to one in which it is controlled completely by the rate of hydrogen transport to the active catalyst site.

Hydrogenation catalysts differ widely in activity and selectivity, with these characteristics determined mainly by the major metal component. Both activity and selectivity are influenced by conditions of temperature, pressure, and degree of agitation.

Solvents may be used to increase ease of handling and catalyst recovery, moderate exothermic reactions, increase rate and selectivity, and permit hydrogenation of solid material.

Agglomeration of the catalyst is a problem detrimental to the hydrogenation process which may be overcome by changing the pH of the medium, changing the solvent, the solvent-substrate ratio, or the catalyst support. Catalytic poisoning is another problem which can affect hydrogenation.

It is difficult to predict a regeneration technique suitable for specific catalyst. Eventually, a catalyst reaches a point after which it can no longer be sufficiently regenerated.

Small quantities of substances which favorably affect catalyst life, activity, or selectivity may be termed promoters. Although the effect of a promoter depends on the reaction in which the catalyst is used, there is little existing theory on which to base successful choice of a promoter.

8.4.2 Recycle, Recovery, and Reuse Applications: Inorganics

Wilson (1971) describes a process in which hydrogen is recovered from gases in which it is concentrated at greater than 20% by volume. In this process, a hydrogen-extracting aromatic hydrocarbon is introduced countercurrently to the system. Following hydrogenation, the aromatic hydrocarbon is sent by countercurrent flow to a dehydration catalyst zone. The process results in the recovery of a hydrogen-containing gas of 90 volume %.

Sulfur recovery may be effected through implementation of a process described by Rowland (1970). Sulfur present in tail gas is converted to pure hydrogen sulfide by hydrogenation under moderate conditions of temperature and pressure. A cobalt molybdate catalyst is effective in reacting water vapor with CO to COS and CS_2 to form H_2S. Following hydrogenation and cooling, H_2S is removed and converted to sulfur by the Stretford process, or by recycle to the reaction furnace of a sulfur plant.

8.4.3 Recycle, Recovery, and Reuse Applications: Organics

Substitute natural gas may be produced from whole crude oil fractions boiling above naphtha. Components of the process include a reaction system, a quench system, gas purification and secondary hydrogenation areas, and a gas drier. Preheated oil and hydrogen gas are reacted in a fluidized bed of coke particles, resulting in the production of a rich gas with a concentration of methane and ethane. The gas is quenched with a circulating stream of light aromatic to effect separation of liquid products. Hydrogen sulfide is removed from the rich gas in an absorption-stripping system and converted to elemental sulfur in a Claus plant.

In the secondary hydrogenation section, purified gas is contacted with a catalyst in a fixed bed reactor. Ethane contained in the gas reacts with hydrogen to produce methane. In cases in which there is an excess of hydrogen to ethane, carbon dioxide or hydrocarbons such as liquified petroleum gas are added upstream of the secondary hydrogenation step, resulting in product gas containing less than 5 mole % hydrogen (McMahon, 1972).

Diolefins and olefins may be selectively removed from the product gasoline obtained in light olefin manufacture resulting in the recovery of usable hydrocarbons. Parker (1967) describes a process in which an aromatic hydrocarbon feedstock containing diolefins, mono-olefins, and sulfur contaminants is hydrogenated at a temperature of 200-500°F with a composite catalyst of lithium in palladium-alumina to convert the diolefins to mono-olefins. The effluent is separated and an aromatic hydrocarbon is then hydrogenated at a temperature of 550-750°F with a conventional desulfurization catalyst to saturate olefins and convert sulfur compounds to hydrogen sulfide. Hydrocarbons suitable for gasoline blending and aromatic hydrocarbons suitable for solvent extraction are recovered as separate product streams.

8.5 CHEMICAL REDUCTION

Chemical reduction is a widely used industrial waste treatment process, which has the potential for recovering pollutants such as metals. This process is primarily applied to the control of hexavalent chromium in the plating and tanning industries.

Reduction and oxidation reactions take place concommitantly and so the overall process is referred to as an oxidation-reduction (redox) reaction. In a redox reaction, the oxidation state of at least one reactant is raised while that of another is lowered. In the following reaction:

$$2H_2CrO_4 + 3SO_2 \rightleftarrows Cr_2(SO_4)_3 + 2H_2O \qquad (8.4)$$

hexavalent chromium (oxidation state 6+) is reduced to trivalent chromium (oxidation state 3+), while sulfur is oxidized with an increase in its oxidation state from 2+ to 3+. Sulfur compounds and base metal components such as those of iron, zinc and sodium are the more common reducing agents.

8.5.1 Limiting Technology

Most of the applications of chemical reduction technology to industrial waste treatment to date have been for dilute waste streams. Chemical reduction has limited applicability to slurries on sludges in their original form because of the difficulties of achieving intimate contact between the reducing agent and the pollutant to be removed. One of the disadvantages of chemical reduction is that it introduces new metal ions into the effluent stream. If the level of these new contaminants is high enough to exceed effluent guidelines, additional treatment will be required, adding more cost to the overall treatment.

8.5.2 Recycle, Recovery, and Reuse Applications

The two most common applications of chemical reduction processes are the removal of hexa chromium from plating and tanning industries and the removal of mercury from caustic/chlorine electrolysis cell effluents.

In plating and tanning industries, sulfur dioxide is mostly used for reducing hexavalent chromium to trivalent chromium, which is then precipitated as $Cr(OH)_3$ with either lime or sodium carbonate. The waste is then subjected to sedimentation, which separates the solids portion.

The reaction equations are as follows:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \qquad (8.5)$$

$$2H_2CrO_4 + 3H_2SO_3 \rightleftarrows Cr_2(SO_4)_3 + SH_2O \qquad (8.6)$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightleftarrows 2Cr(OH)_3 + 3CaSO_4 \qquad (8.7)$$

The precipitated chromium can be potentially recovered for further use.

For removal of mercury from industrial effluents, a caustic solution of sodium borohydride (NaBH) is mixed with the wastewater, which results in the reduction of ionic mercury to metallic mercury. The latter precipitates out of solutions, which can be recovered for recycle.

Sodium borohydride is also used for reducing lead and silver compounds from industrial effluents. These compounds are usually reduced chemical metals, which can be precipitated, settled and recovered for reuse.

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CHAPTER 9

SECTION II

PHYSICAL DISPERSION AND SEPARATION

9.1 INTRODUCTION

The sixth and final chapter of this report will examine the "Recycle, Reuse and Recovery Applications" of various physical dispersion and separation processes. The processes included in this chapter are:

1. Filtration of Liquids
2. Filtration of Gases
3. Flotation
4. Liquid-Liquid Extraction

In addition to the Recycle, Reuse and Recovery Application section for each process, a brief process description will be included and, in many cases, a limiting technology statement will also be given.

9.2 FILTRATION OF LIQUIDS

Filtration is a physical process, in which solids suspended in a liquid are separated from that liquid by passage through a previous medium, which separates and retains either on its surface or within itself, the solids present in the suspension. In all filtration processes, a pressure differential is induced across upon the required magnitude of the pressure differential, one or more of four types of driving force may be employed: gravity, vacuum, pressure, or centrifugal. During the filter operation, a gradual pressure drop occurs due to clogging or breakthrough of suspended matter. When the pressure drop reaches a predetermined after pretreatment by air scrubbing or a hydraulic surface wash.

The filter media presently available in the commercial market can be divided into three general classes (Arthur D. Little, Inc., 1976):

1) A thick barrier composed of a layer of granular media such as sand, coke, coal, or porous ceramics,

2) A thin barrier exemplified by a filter cloth on filter screen,

3) A thick barrier composed of a disposable material such as powdered diatomaceous earth or waste ash.

The mechanics by which the particles are removed in the filters are complex. In surface filters, the predominant mechanism is usually simple mechanical straining. However, in deep-bed filters, the mechanisms can include mechanical straining coupled with gravitational settling, diffusion, interception, inertial impaction, electrostatic interactions, chemical bridging, and specific adsorption phenomena within the filter medium (Weber, 1972).

Basically, there are two types of filtration processes. Surface filters perform cake filtration, in which the solids are deposited in the form of a cake on the upstream side of a relatively thin filter medium. Deep filters are used for deep-bed filtration in which solids deposit within the medium. Formation of a cake on the surface of a deep bed is undesirable (Svarovsky, 1979). Surface filters are normally used for suspensions with more than one percent solids whereas dilute suspensions are treated by deep-bed filters.

The filter units generally consist of a containing vessel, the filter media, structures to support or retain the media, distribution and collection devices for influent, effluent, and wastewater flows, supplemental cleaning devices, and necessary controls for flows, water levels, or pressures. Some of the more significant alternatives in filter layout are discussed in an EPA process design manual for suspended solids removal. (U.S. EPA, Jan. 1975).

A wide variety of filtration devices are commercially available. However, they can be classified under the following categories having similar characteristics:

1. Deep Bed Filters:

Deep bed filters were originally developed for potable water treatment but presently they are increasingly used for industrial and municipal wastewater treatment. The filter bed is usually contained within a basin or tank and is supplied by an underdrain system which allows the filtered liquid to be drawn off while retaining the filter medium in place. The most common configuration of a deep-bed filter is the downflow gravity design. The solids concentration in the feed should be less than about 0.1% by volume in order to keep down the number and volume of the washer. The most common example of deep-bed filters is the granular media filters, which use a bed of granular particles (usually sand from 0.4 to 2.5 mm in size), as the filter medium. The use of dual or multi-media filters is becoming increasingly common. Such filters have coarse material of low density for the top layer and progressively finer materials of increasing density for the lower layers. An example of triple media is a combination of anthracite, filter-sand, and garnet.

Deep-bed filtration is most often operated as a batch process. However, continuous filters which continuously backwash a portion of the medium are not uncommon. Some examples of such filters are hydromation in-depth filters, radial-flow filters, and traveling backwash filters. (U.S. EPA, Jan. 1975).

2) Pressure Filters:

Pressure filters can treat feeds with concentrations up to ten percent solids. Pressure filters may be grouped into two categories, plate and frame filters presses and pressure vessels containing filter element

(Svarovsky, 1979).

The conventional plate and frame press consist of a series of plates and frames, alternately arranged in a stack and pressed together with hydraulic or screw-drawn rams. The plates are covered with a filter cloth. The slurry is pumped into the frames and the filtrate is drained from the plates. Filter media for plate and frame presses include various cloths, mats, and even paper. The second category of pressure filters includes a number of available designs that feature a pressure vessel containing filter elements. Some examples in this category of filters are: rotary-drum pressure filters, cylindrical element filters, vertical-tank vertical-leaf filters, horizontal tank vertical-leaf filters, and horizontal-leaf filters (Svarovsky, 1979). A few of the above-mentioned filters are used for dewatering purposes and are discussed in a separate report.

In addition to the filters discussed above, there are centrifugal filters, fixed-bed centrifugal, moving-bed centrifuges, and cartridge filters, which are used in industrial wastewater treatment.

9.2.1 Limiting Technology: Filtration of Liquids

Filtration is a well developed process and most of the problems with this process seem to be associated with the filter operation. The major problem with filter operation is maintaining the filter bed in good condition. Inadequate cleaning results in a thin layer of compressible dirt or flue around each grain of the medium. As the pressure drop across the filter medium increases during the subsequent filter run, the grains are squeezed together and cracks form in the surface of the medium (Weber, 1972). These dirty grains become larger in size gradually and sink to the bottom of the filter, reducing the filtration effectiveness.

9.2.2 Recycle, Reuse, Recovery Applications: Filtration of Liquids

Filtration has been used for treatment of innumerable types of industrial wastewaters. Multimedia filtration is commonly used for removal of the metal precipitates from wastewater after it has been subjected to precipitation, flocculation, and sedimentation. Filtration is also used for dewatering of waste sludges from biological treatment systems.

9.3 FILTRATION OF GASES

Filtration is the oldest method used for removal of suspended materials in gases. It operates on the principle of passing dust-laden gases through porous filter media in which the dust is trapped. Filtration methods form one of the largest families of gas cleaning devices, and can be applied over a wide range of conditions.

All filter media collect dust by a combination of effect summarized below:

1. Particles larger than the pore size of the medium will be separated due to a sieving effect of the medium.

2. Particles may be separated by an inertial effect created by the many changes of direction the particle must undergo in passage through a tortuous filter medium.

3. Fine dust particles may be deposited on the filter medium as a result of the electrostatic charge which they often carry.

4. Sub-micron size particles having a weight similar to that of the molecules of carrier gas will not be separated by inertial effects. They will instead be subject to Brownian movement, and as a result will be brought into close proximity to the filter medium, where they are deposited and held

by electrostatic and molecular forces.

5. Particles smaller than the filter pores will be efficiently retained by a layer of dust which accumulates on and within the filter material. This layer will create a pressure drop across the filter which must be taken into account during plant design.

Filter media can be broadly considered under three headings:

1. Gravel or Sand Aggregate Bed
2. Porous Paper and Fibrous Mats
3. Woven and Felted Fabric Filters

Aggregate bed filters consist of uniform size particles such as sand or gravel. These filters are not currently in wide use for industrial gas cleaning. Gas cleaning efficiency increases with decreasing size of aggregate and with increasing depth of bed. In one application, beds of fine sand two meters deep were used to filter particles of radioactive material from exhaust gases. These filters were found to be over 99 percent effective even on submicron particles.

The aggregate filter is simple in design and can be used at elevated temperatures. When such filters are used on gases with high moisture content, it is necessary to keep the aggregate above dewpoint when dust-laden gases are introduced. This prevents blockage of the bed by wet dust which is not dislodged by normal cleaning methods.

Fluidized beds of aggregate have generally been found to be somewhat low in efficiency (approximately 80 percent) due to re-entrainment of dust caused by motion of the bed.

Paper filters, due to their relatively poor mechanical properties, are normally used at lower temperatures where dust concentrations are less than 5 $mg\text{-}m^{-3}$. These filters are not normally used for industrial pollution control requirements.

Fibrous mat filters consist of fibers of a natural, synthetic, or glass nature. The fibers may be mounted in mat form between supporting sheets of gauze or perforated metal. Filter characteristics vary according to depth of filter, material of construction, and the density of filter packing. Fibrous filters remove coarser material, but when pressure losses rise to 15-30 cm W.G. due to packing density, high collection efficiencies are possible for materials as fine as the sub-micron acid mist originating from sulphuric acid plants.

Because of the many different kinds of filter material available, fibrous filters are useful over a wide range of operating variables such as temperature and corrosivity. Their application is limited, however, to streams containing relatively low concentrations of dust. When resistance rises to an unacceptable level, they must be cleaned or replaced.

Fabric filters take the form of woven fabric or felted materials manufactured from natural or man-made fibers. They are capable of treating large gas volumes with high dust concentrations on a continuous basis. The design filter rate is usually in the range of a pressure loss of 6-12 cm W.G., depending on whether the cloth is clean or has a layer of dust deposited on it.

Woven cloth has relatively large gaps where its threads cross, which may also be large in comparison with the particles to be caught. This will result in low efficiency with new filter bags, but as the dust builds up and blocks the holes, efficiency improves. Eventually, filtration efficiency is determined not by the filter, but by the dust layer, allowing particles below 1 meter to be caught.

Felted cloth avoids the problem of regular holes, since its fibers are laid in random fashion. The pile on its surface also increases effective filtering area, although this pile makes effective cleaning more difficult. Synthetic fibers, lack natural felting properties, and must undergo a process in which a felt is artificially induced by passing barbed needles through the fiber mat. It has been reported that needle fibers combine the high filter rate of felts with the property of being easy to clean.

The range of temperature over which fabric filters can be used is restricted. The maximum operating temperature for silicone coated glass fiber filters is 270°C, and those for other materials commonly in use, such as teflon, nylon, wool, and cotton are lower. New materials are being developed which are expected to extend this temperature range; stainless steel is reported to have an operating temperature which exceeds 400°C. These new materials are expensive, however, a further limitation on operating temperature is that the dust remains dry and flows freely. If the gas temperature falls below the dewpoint, the filtered dust will become caked on the fibers, eventually resulting in blinding of the media.

Removal of dust from baric filters is accomplished by flexing or collapsing the bag and blowing the accumulated dust from its surface.

Corrosive elements of gas and dust, as well as sharp edges on the dust particles, can result in rapid failure of the filter. Preferably, filter material should be chosen which has a life of several years. Another operational problem may arise when explosive mixtures are filtered due to the electrical insulating properties of natural and synthetic fibers. If the electrostatic charge is allowed to build up, it creates an increase in voltage which may cause arcing through the gas. Explosion or fire may result. This problem can be avoided by introducing a small quantity of conducting fiber such as metal into the cloth in order to give it anti-static properties.

Efficiency for fabric filters is always high (Parker, 1978). Collection efficiencies in excess of 99.5 percent are normal. Fabric filters are commonly used for control of dust concentrations in the range of $10^2 \mu g/m^3$ (urban atmospheric dust) to $10^3 \mu g/m^3$ (pneumatic conveying). They provide effective removal of particles ranging in size from submicrometer fumes to 200μm powders (Billings, 1977).

9.3.1 Limiting Technology

Filter media used for removal of suspended materials in gases can be broadly grouped into three categories: gravel or sand aggregate beds; porous paper and fibrous mats; and woven and felted fabric filters.

The aggregate filter is simple in design and can be used on dust-laden gases with high moisture content, it is necessary to keep the aggregate above dewpoint to prevent blockage of the bed by wet dust which is not dislodged by normal cleaning methods. Fluidized aggregate beds may have low efficiency due to re-entrainment of dust caused by motion of the bed.

Paper filters have poor mechanical properties, and are not normally used for industrial pollution control.

Fibrous filters are useful over a wide range of operating conditions such as temperature and corrosivity due to the many types of filter material available. Their application is limited to streams containing relatively low dust concentrations.

Fabric filters are capable of treating large gas volumes with high dust concentration on a continuous basis. With woven cloth filters having large holes, filtration efficiency is determined ultimately by the dust layer which collects on the filter, and not by the filter itself. The use of felted cloth eliminates the problem of regular holes, since its fibers are laid in random fashion.

The temperature range for the use of fabric filters is restricted by the type of filter material. New materials are being tested which are expected to extend the range of operating temperatures to 400°C and above. The gas temperature must stay above dewpoint to eliminate the problem of dust caking on the filters.

Corrosive elements of gas and dust and sharp dust particles edges can cause rapid filter failure. An additional operational problem is the building up of electrostatic charge on the filter. This must be prevented in order to prevent explosion of gas or an outbreak of fire. Introduction of a small quantity of conducting fiber into the filter cloth will give it antistatic properties.

Collection efficiencies in excess of 99.5 percent are normal for fabric filters.

9.3.2 Recycle, Recovery, and Reuse Applications: Organics

Due to the shortage of oil, the recycling of asphaltic pavement became an issue of interest. A problem which occurs in trying to convert conventional asphalt plants to plants which have recycle capabilities is the formation of fine particulate smoke which occurs when crushed pavement is subjected to temperatures necessary for recycling. At these temperatures, the asphalt begins to crack and release hydrocarbon vapor which condenses into submicron droplets. These oily droplets are poorly collected by baghouse filters and venturi scrubbers, devices currently in use at asphalt plants.

The electrofluidized bed (EFB), designed for high efficiency collection of submicron particles, was tested on emissions from an asphalt recycling plant. The hydrocarbon pollutant is collected on sand which is then removed from the bed in its fluidized state and added to the asphalt product. Efficiencies of collection in excess of 98 percent were reported for submicron particles in beds having unfluidized depths of 8-12 cm, using sand having a mean diameter of 2 mm. Using this procedure, it was possible to combine collection of submicron particles at high efficiency with the recycling and reuse of the collected hydrocarbons and the filter sand (Zieve, et al. 1978).

9.3.3 Recycle, Recovery, and Reuse Applications: Inorganics

In certain manufacturing operations involving expensive water insoluble dusts or powders in which excess material is normally exhausted as part of the operation, it has been found to be economical to collect exhaust material in a filter from which the retained materials can be recovered. Such a method is used for collecting phosphor particles produced in forming color cathode ray tubes by the dry phosphor technique.

Excess phosphor particles are collected from the exhaust atmosphere by passing exhaust air through several filter media. The first filter is normally coarse woven, and is cleaned by vacuuming, shaking, or beating. The remaining superfines are then collected by filters made of materials such as cellulose, glass, or plastic in the form of fibrous compactions. These filters are not suited to mechanical removal of phosphor without destruction. In some cases, the phosphor particles have been dissolved for reclamation by organic solvents or similar chemicals. This is an expensive process, however, and caustic solvents may be detrimental to the phosphor (Warner, 1971).

Warner (1971) developed a decomposable filter for collecting water in soluble particles of gasborne materials. The filter medium is comprised of water soluble organics which are stable in an environment have ambient relative humidity less than 90 percent and an ambient temperature under 100°C. Particluate material is reclaimed by dissolving the filter in water. The particulate matter is allowed to settle, and is recovered by decanting the supernatant. Alternatively, the mixture of particulate and dissolved filter medium is passed through a recirculating filter having a core of perforated discs upon which the particulates are collected. Heated air is then forced through the filter in a reverse manner to dislodge and dry the collected particulate.

9.4 FLOTATION

Flotation is a unit operation used to separate solid or liquid particles from a liquid phase. Separation is brought about by introducing fine air bubbles into the liquid phase. The bubbles attach to the particulate matter and the buoyant force of the combined particle and gas bubbles is large enough to cause the particle to rise to the surface (Metcalf and Eddy, 1980). Three methods of introducing gas bubbles have been shown to create bubbles sufficiently fine for flotation of suspended solids in municipal and industrial wastewaters.

1) Injection of air while the liquid is under pressure, followed by release of the pressure (dissolved air flotation).
2) Aeration at atmospheric pressure through revolving impeller or porous media.
3) Application of a vacuum to the wastewater, which is saturated with air at atmospheric pressure.

In biological treatment systems, biological flotation occurs when the gases formed by natural biological activity attached to the suspended solids and rise upwards through the liquid. For any of these systems, the degree of removal can be enhanced through the use of various chemical additives (Metcalf and Eddy, 1980).

9.4.1 Dissolved Air Flotation

In dissolved air flotation (DAF) systems, bubbles of size 100μ or less are obtained by dissolving air in water at an elevated pressure and then reducing the pressure of the air-water mixture. The water is pressurized in the range of 40-80 psi and a stream of air is injected into the pressurized water and retained in a tank under pressure for several minutes to allow time for the air to dissolve. At $60^{\circ}F$, about one cubic foot of air is used for each 100 gallons of air-charged water (U.S. EPA, Jan. 1975). The air-charged water then passes through a pressure reducing valve into the flotation treatment tank. The reduction in pressure causes the solubility of the air to decrease and excess air comes out of solution in the form of minute bubbles (average size 18μ). These bubbles attach to the sludge particles and increase their bouyancy, causing them to float to the surface. In some cases a portion of the effluent (15-120 per cent) is recycled, pressurized and semi-saturated with air (Metcalf and Eddy, 1980).

A coagulant aid may be used with a DAF unit in order to 1) increase the allowable solids loading; 2) increase the percentage of floated solids; and 3) improve the clarity of the subnatant.

9.4.2 Air Flotation

In air-flotation systems, air bubbles are formed in the flotation tank by a revolving impeller or through diffusers. These systems are not common in industrial wastewater treatment operations.

9.4.3 Vacuum Flotation

In vacuum flotation systems, the wastewater is initially saturated with air and a partial vacuum is then applied which causes the dissolved air to come out of solution as minute bubbles. These bubbles attached to the sludge particles in wastewater and rise to the surface to form a scum blanket, which is easily removed by a skimming mechanism.

9.4.4 Recycle, Recovery and Reuse Applications

Flotation is a process of ore concentration developed and used principally by the mineral industry. In wastewater treatment it is mostly used to remove suspended matter and concentrate biological sludges. There have been a number of other applications of flotation in the waste treatment area.

In a variation of the process called precipitate flotation, precipitates can be collected on the top of the flotation tank and recovered as a froth concentrate (Arthur D. Little, Inc., 1976). In this application, the metal to be removed from solution is precipitated. Another possible application of precipitate flotation is the flotation of complexed cyanide (for example, ferrocyanide precipitate) as a means of removing cyanide from solutions (Grieves and Bhattacharya, 1969).

In another variation of the flotation process, known as ion-flotation, a surfactant ion of opposite charge to the inorganic ion removed from solution is added in stoichiometric amounts. The surfactant, which must exist in solution as simple ions, reacts with the inorganic ion to form an insoluble "soap" which is raised to the surface with a bubbling action. Rubin et al. (1966) reported removal of dissolved copper with sodium lauryl sulfate using the ion flotation process.

The insoluble metal precipitates formed during ion and precipitate flotation processes can be further subjected to treatment for recovery of metals.

The flotation process is used for recovery of copper from the slag generated in smelters (Matheson, et al. 1976). Flotation is also used for removal of oil from industrial wastewaters such as those from refineries.

9.5 LIQUID-LIQUID EXTRACTION

Liquid-Liquid extraction has become an important separation technique used by various industries either to remove small amounts of an impurity from a product stream or to separate products. This technique is considered to be a viable waste treatment process for selected waste streams, where recovery of material is possible. The major applications of this process in wastewater treatment engineering are 1) recovery of phenol and related compounds from wastewaters and 2) removal of water soluble solvents such as alcohol from wastes containing mixed chlorinated hydrocarbon solvents.

Liquid-Liquid extraction, hereinafter referred to as solvent extraction, involves separating the components of a liquid mixture by the addition of another liquid referred to as the solvent which is immiscible or only partially miscible) with the initial phase. The solvent is chosen such that one of more of the components of the original solution, called the solute. will transfer preferentially into the solvent phase, leaving the others behind in the so-called "raffinate." The product of the desired solute in the solvent is called the extract. At equilibrium, the ratio of the concentrations of solute in the extract, y, and raffinate, x, phases is called the distribution coefficient D. The coefficient is used as an indicator of the ability of a solvent to extract a particular solute.

The proportion of solute recovery in a single equilibration depends on both the distribution coefficients for that solute and the relative amount of solvent used. To obtain a high recovery without using an excessive amount of solvent (with the corresponding production of a very dilute extract), most processes employ multistage countercurrent contacting (Hanson, 1979).

The purity of the initial extract is often enhanced by scrubbing with a suitable immiscible phase such that bulk of the desired solute in the solvent phase is retained while the impurities are washed out. The scrub feed is usually based on the same solvent as the original feed and the scrub raffinate is then combined with the main feed to permit recovery of any of the desired solute which may have transferred.

The solute may be removed from the extracted solvent by a second solvent extraction step, distillation, or an alternative process. Depending upon cost considerations, solvent recovery from the treated stream may be advantageous. This may be accomplished by stripping, distillation, adsorption, on other suitable process. A typical single-stage solvent extraction process is illustrated in Figure 6.1.

Various devices were developed through the years to establish phase equilibrium rapidly and thereby accomplish solvent extraction based on a combination of capital and operating costs. Several discussions (Oberg and Jones, 1963; Bailes, et al. 1976; Reissinger and Schroeter, 1978a, 1978b) on the various extraction devices in use are available in the literature.

The extraction devices have two things in common; first, they generate a large amount of interfacial area between the two liquid phases mostly by dispersing one phase in the other and second, they impart mechanical energy into the system by means of agitation to maintain a degree of turbulence in one or both phases (Eckert, 1976). An overall review of industrial extractors and their relationship to different extraction processes is given in Figure 6.2. A thorough discussion of the different types of extractions in Figure 6.2 is given by Reissinger and Schroeter (1978a, 1978b).

There is no general guide to contactor selection. Most of the contactors available in the market may be used for simple processes and a final choice will depend on the results of an economic evaluation of available options as well as the consideration of local factors such as space availability (Bailes, et al. 1976). Reissinger and Schroeter (1978a, 1978b), have attempted to establish a selection procedure based on the use of a diagram into which the most important parameters have been incorporated. The suggested scheme may only be used as a rule of thumb, however. The final design of a specific solvent extraction unit of a new application should be preceded by detailed laboratory tests as well as technical and economic comparisons with competing processes.

9.5.1 Limiting Technology

Liquid-liquid (solvent) extraction is a well established process which have relatively few insurmountable technical problems. The problems associated with the application of solvent extraction to recovery of by-products from waste streams are basically related to the difficulty in selecting solvents and a contactor, which are, in combination, capable of producing the desired results.

9.5.2 Recycle, Recovery and Reuse Applications

Liquid-Liquid extraction is being used in both commercial processing and wash applications. The following are the major waste treatment applications:

1) Removal and recovery of phenol and related compounds from petroleum refinery waste (Anonymous, 1973; Coke-oven liquors, Carbone, 1967;

Aver et al. 1969) and phenol resin plant effluents (Wurm, 1968).

2) Removal and recovery of water-soluble solvents such as alcohol from wastes containing chlorinated hydrocarbon solvents.

3) Extraction of thiazole-based chemicals (Anonymous, 1970), acetic acid (Himmelstein, 1974) and Salicylic acid (Anonymous, 1970).

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